The Structure of Trimethylacetic Acid in Condensed Phases as Revealed from Dielectric Studies

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Introduction

Trimethylacetic acid, $(CH_3)_3CCOOH$, solidifies at 35.2°C, with a very small entropy of fusion, $\Delta S = 2.7$ e.u., as estimated by Pirsch,[1] and gives a cubic crystal. This crystal transforms into another phase of lower symmetry at 7°C with a greater heat of transition. These properties of this compound are very peculiar in contrast to those of the usual lower fatty acids. Formic acid,[2] for instance, has a crystal structure made up of infinite chains of hydrogen-bond between the molecules, and its entropy of fusion is 10.8 e.u.[3]

Timmermans[4] pointed out from these facts that this cubic phase was a kind of plastic crystals, implying that the molecular arrangement in this crystal may have some kind of disorder. This point of view was supported by an X-ray investigation.[5] Our knowledge about the detail of this disordered structure is, however, still quite obscure, and it is the purpose of this paper to add some information to this problem as the result of our dielectric measurements.

Experimentals

1) Purification of the Material.— Trimethylacetic acid was synthesized by the method given in "Organic Syntheses".[6] Special care was taken in drying, so that the sample used was free from moisture as completely as possible. After repeated distillations at low pressure and subsequent recrystallizations, the sample was dried in a desiccator with phosphorus pentoxide for about five days. The material was then sublimed in vacuum of about 10^{-5}mm Hg, and condensed slowly into the measuring cell (shown in Fig.3) in the same vacuum system. The apparatus is shown in Fig.1. The sample thus purified melts sharply at 35.2°C. During the observation there was no noticeable decrease of melting point.

2) Electrical Circuit for the Dielectric Measurement.—Since the amount of the sample obtained was very small, it was necessary to measure small capacities of about 5 pF in the low frequency region. For this purpose we used a revised circuit of the transmitter method shown in Fig.2. With this circuit we were able to observe the capacity from 20 pF to 0.2 pF in the frequency range from 300 cycle to 100 k.c. and the conductance below 10^{-6}

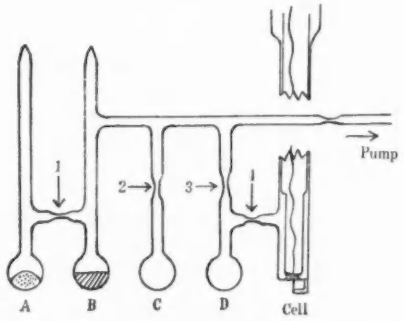

Fig. 1. The process of purification. After distillation and recrystallization, the sample is placed in B with phosphorus pentoxide in A for about five days. Then A is cut off, the system evacuated and half of the sample is sublimed into C, which is cut off. The middle portion of the sample in B is sublimed into D. D and the cell are cut off, and the sample is poured into the Cell. Then D is cut off from the cell.

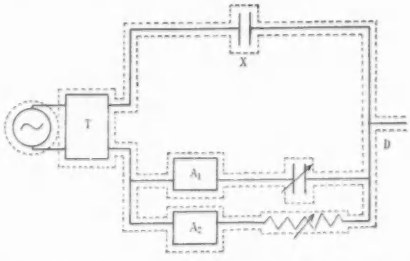

Fig. 2. Electric circuit. T: shielded transmitter. A_1 and A_2 atenuaters. D: detector of zero voltage. X: measuring cell electrode.

1) J. Pirsch, *Ber.*, **70**, 12 (1937).
2) F. Holzberg, B. Post and I. Fankuchen, *Acta Cryst.*, **6**, 127 (1953).
3) Calculated from the values in the "Physico-chemical Constants of Pure Organic Compounds" by J. Timmermans, Elsvier Publishing Co., Inc., (1950), p.379.
4) J. Timmermans, *J. chim. phys.*, **35**, 331 (1938).
5) Y. Namba and T. Oda, This Bulletin **25**, 225 (1952).
6) "Organic Syntheses," Coll. Vol., I., A. H. Blatt, Ed., John Wily and Sons, Inc., New York, N. Y., (1947), p.524.

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mho, within the accuracy of ±1% in terms of the absolute value of the dielectric constant. This was examined preliminarily by the measurements on benzene, carbon disulfide, and chloroform. The measurement of the dielectric constant and loss between the frequency range from 100 k.c. to 3 m.c. was carried out by the Q-meter, using the variable precision condenser.

3) Direct Current Conductivity.—The conductivity was measured in the usual way, using the cell shown in Fig.3. The applied voltage was about 10 volts, and a galvanometer of sensitivity 10^{-11} amp./mm. was used. There was no detectable adsorption current.

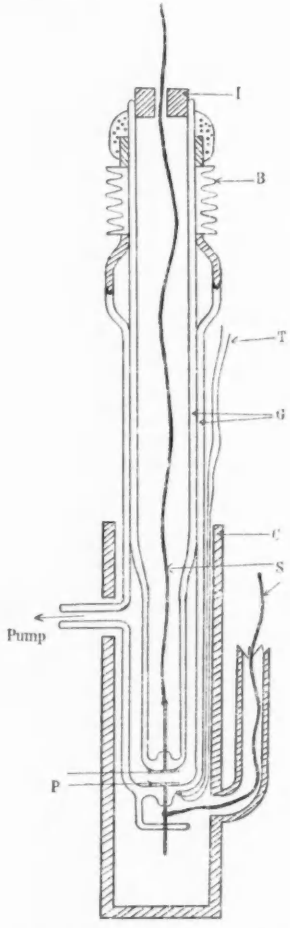

Fig. 3. The measuring cell. G: glass. B: bellows. P: platinum circular parallel electrodes. C: copper block. T: Cu-constantan thermocouple. S: electric leads. I: Polystyrol insulator. C and T are earthed.

4) Electrode Cell.—To facilitate the measurements in vacuum or under dried conditions and to cover a wide temperature range, we used the cell shown in Fig.3, bellows being used in order to keep close contact between the electrodes and the sample during volume change in the solid state. This cell was used for the measurements of both the dielectric constant and the conductivity.

Result

The values of the dielectric constant were obtained in the temperature range from −30°C to +70°C, (shown in Fig. 4). The dielectric constant of tae room temperature phase was found to be have a very small value of 2.62, compared with those of formic and acetic acid.[7] The dielectric loss was of the same order as that of the glass cell, or even smaller and hence this compound falls into the category of insulator. In the frequency range we have studied, there was neither change in the dielectric constant nor loss exceeding the experimental error.

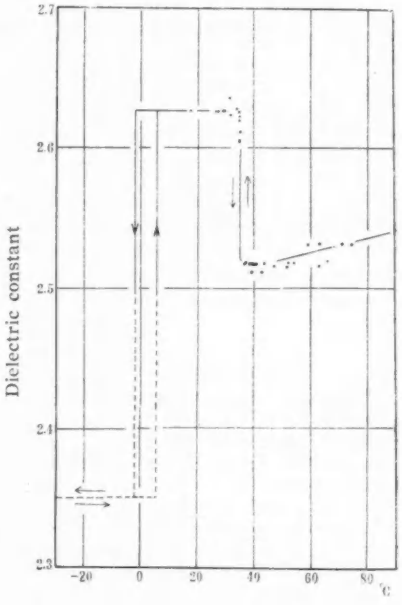

Fig. 4. The dielectric constant vs. temperature curve. The dotted line shows the apparent values of dielectric constant.

On cooling, the dielectric constant increases at the solidifying point. The molecular polarization of both the solid and liquid states near the melting point calculated from the observed values of the dielectric constant and density shows almost the same value, about 38 cc. This will indicate a similarity in the molecular arrangements of the liquid and the cubic modification. This point

of view is also strengthened by the small value of the entropy of fusion. In both states, the value of the dielectric constant is a little higher than the square of the refractive index ($n_D^{20}=1.462$). This difference may be considered as a part of atomic polarization due to the hydrogen-bond, which makes the molecular association possible. The contribution from the orientation polarization is considered to be small.

According to Onsager-Kirkwood's theory,[8] the result given above will indicate that this compound in the two phases, should be composed of nonpolar molecular units, and there seem to be few possibilities of forming chain-like structures.

A reliable value for the dielectric constant of the low temperature phase was not obtained. At the transition point -2°C, the initially transparent crystal with no crack or void becomes suddenly opaque, accompanied by a large volume contraction $\Delta V=10.45$ cc./mol. However, we were able to obtain apparent values of the dielectric constant with powdered crystals at temperatures above and below the transition point. On heating and cooling, the values of the dielectric constant changed almost reversibly. As shown in Fig. 4, the dielectric constant decreases at the transition point and this decrease could be interpreted either by a smaller value of the dielectric constant in the low-temperature modification, or by a kind of preferred orientation of small crystals. The dielectric constant of the cubic phase remained almost constant with varying temperature, while in the liquid state, it has the positive temperature coefficient, contrary to the usual molecular crystals. This might mean a slight increase of the number of the single molecules or the polar association of molecules with increasing temperature. The direct current conductivity (note Fig. 5) showed strikingly small value, being the same magnitude as those of insulators. The hydrogen atoms in the acid radical at lower temperatures, seem not to play a role as the charge carrier and are supposed to be immobile in the stable non-polar molecular units, forming the closed intermolecular hydrogen-bond.

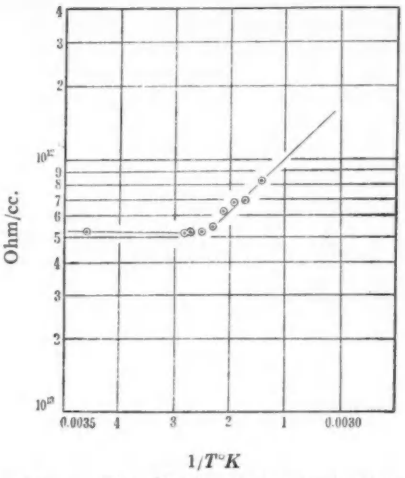

Fig. 5. The direct current conductivity vs. reciprocal temperature curve.

Discussion of the Structure

By the X-ray crystallographic investigation, the crystal shows only three kinds of reflection of face-centered cubic symmetry, $a_0=8.82\pm0.03$Å, containing four molecules in the unit cell. From the symmetry consideration, it was concluded that the structure allows the disordered orientation of molecules.[5]

If we assume the non-polar polymer discussed in the preceeding section to be a dimer, it is possible to obtain a reasonable interpretation of the disordered structure of this crystal. Suppose that the center of mass of each molecule (shown in Fig.6) occupies each lattice point, and this molecule associates with one of the twelve first nearest neighboring molecules by the hydrogen-bond to form a dimer, the four oxygen atoms being coplanar. The shortest intermolecular distance between the oxygen atoms within this dimer comes out to be 2.7 Å, which is a plausible value for the O—H···O hydrogen-bond distance of the fatty acids. We may further assume that this dimer is fairly stable, in view of the fact that the dispersion in dielectric constant is absent. Thus the single molecule may not undergo a dynamical rotation, but the dimer moves as a whole, accompanied by the migration of vacancies which will amount to comparatively large numbers as is seen from the difference of the calculated and observed densities 0.99 and 0.973 at 12.4°C respectively. Such a migration seems to be quite possible, considering the numerical value of the nearest distance of approach between the dimers as is estimated from the van der Waals radii. It is also plausible that the methyl or *t*-butyl radicals, rotate around their C-C bonds and their details would be

7) J. F. Johnson and R. H. Cole, *J. Am. Chem. Soc.*, **73**, 4536 (1951). W. Dannhauser and R. H. Cole, ibid., **74**, 6105 (1952). C. P. Smyth and H. E. Rogers, ibid., **52**, 1824 (1930).

8) See for instance "Theory of Dielectrics" by H. Fröhlich, Oxford Press, (1949), p.104.

clarified through further investigations such as nuclear magnetic resonance absorption. Thus it is concluded that the crystal is made up of dimers orientating randomly, the most stable configuration being such that their axes point to one of the twelve [110] directions, keeping the center of mass of each molecule on the lattice site.

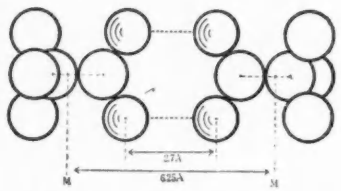

Fig. 6. The schematic model of the dimer of trimethylacetic acid. The steric configulation of *t*-butyl radicals was assumed arbitrarily.

It is interesting to compare the state of association of this compound with that of formic acid. With formic acid, there will be several steps in degrees of association corresponding to the gas, liquid, and solid states.

On the other hand, there seem to be few differences between the liquid and cubic phases of the present material. The bulky *t*-butyl radical seems to be most responsible for such a peculiar structure and properties of trimethylacetic acid.

Summary

The authors have investigated the electric properties of trimethylacetic acid in the liquid and solid states. From the markedly small values of dielectric constant and conductivity, combined with the results of the X-ray investigation, it is proposed that the crystal of the room temperature phase is composed of nonpolar dimer units having disordered orienation.

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An Equation of State in Analytical Form (Concluded)

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The substances already exemplified for the verification of the author's equation of state, $(p+a/V^{2-\varepsilon})(V-b)=RT$, $a=3p_cV_c^2$, $b=V_c/3$, were all non-polar or slightly polar which yielded to the condition that at their critical points the pressure independent constants, ε's, converged to a universal constant, 0.077 $\pm$0.008 when V_c is expressed in cc./mol., and for these substances his newly defined association degree, A, which is the ratio of the critical factor to van der Waals' critical factor, 8/3,

$$A=\frac{3}{8}\left(\frac{RT_c}{P_cV_c}\right), \text{ and } \frac{RT_c}{P_cV_c}=\frac{2(1+3V_c^2)}{3} \tag{1}$$

was found to be from the lowest values of 1.22–1.29 for non-polar molecules such as He, A, Kr, N_2, O_2, and CH_4 to the highest values of 1.47–1.49 for slightly polar molecules such as $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$, and $CH_3CO_2C_3H_7$[1].

For strongly polar substances such as acetone, lower alcohols, acetic acid, and water, ε's at their critical points always take greater values thus: $(CH_3)_2CO$, $\varepsilon=0.101$; CH_3OH, $\varepsilon=0.139$; C_2H_5OH, $\varepsilon=0.105$; n-C_3H_7OH, $\varepsilon=0.095$; CH_3COOH, $\varepsilon=0.150$; and H_2O, $\varepsilon=0.159$. In these cases, however, A deviates appreciably from the first relation of (1) and takes the form,

$$A=f\cdot\frac{3}{8}\left(\frac{RT_c}{P_cV_c}\right), \tag{2}$$

where f is the deviation factor which may depend upon temperature but can be estimated by putting A from relation (2) into relation (3) in the first report:

$$f=\frac{b}{V-R\beta/\alpha} \tag{3}$$

1) T. Ishikawa, This Bulletin, **26**, 78, 530 (1953); ibid., **27**, 226 (1954); T. Ishikawa, M. Ikeda, ibid., **26**, 516 (1953).

where α and β denote the thermal expansion coefficient and the isothermal compressibility.

Taking f at 20°C into account in the calculation of A, we obtain the values, denoted by the author (20°C) in Table I, in which are also shown the association degrees from other methods by several investigators.

Table I

Association degrees of strongly polar substances

Liquid	Ramsay[2] (20°C)	Traube[3] (15°C)	Bingham & Spooner[4]	The author (20°C)	The author (crit. pt.)
$(CH_3)_2CO$	—	1.53	1.28—1.31	1.78	1.54
CH_3OH	2.32	1.79	1.89—1.93	1.59	1.71
C_2H_5OH	1.65	1.67	1.90—1.98	1.68	1.53
n-C_3H_7OH	—	1.66	1.78—1.92	1.66	1.50
CH_3COOH	2.13	1.56	1.71—1.95	1.75	1.54
H_2O	1.64	3.06	—	(negative)	1.67

As seen from Table I, the author's values are in fair agreement with other values, his method also may well be applicable to computing the association degree of an abnormal liquid.

The only exceptional case, in which f gives a negative value at 20°C and consequently relation (3) fails, is water. At higher temperatures, however, f changes its sign and this substance behaves like a normal liquid. For example, if we adopt from Kennedy's compressibility data,[5] we can see that e.g., at 200 bars f (α and β being calculated by taking $\Delta t=10$°C and $\Delta p=50$ bars) takes 1.144 at 200°C, 1.106 at 250°C, and 1.011 at 300°C. Judging from these values which approach to 1 as the temperature comes near the critical point, 374.23°C, it is highly probable that even for an abnormal liquid like water, this relation (1) holds good at the critical point (the values of the author [crit. pt.] in Table I are A values thus assumed).

Next, we shall examine the applicability of the new equation to water as an example of the most anomalous case.

Among the critical constants, t_c, p_c, and v_c of water, v_c can not be measured directly and has been obtained by graphical extrapolation from the values of the saturation volume of both liquid and vapour above 340°C.[3] Schroer[7] obtained $v_c=2.56-3.57$ cc./g., but Eck[8] obtained $v_c=2.650-3.630$ cc./g. and decide, as the true critical volume, 3.066 cc./g. which is nearly the value appeared in Henning's "Warmetechnische Richtwerte", p. 17 (VDI-Verlag GMBH, Berlin, 1938), from this the author adopted to evaluate A at the critical point for water in Table I.

Trials of the author's equation by Kennedy's data, using $t_c=374.2$°C, $p_c=217.5$ atm., and either of the above extremities of v_c, turned out to give the best constancy for $(2-\varepsilon)$, but with still unsatisfactory results, in the case of $v_c=2.56$ cc./g, the least value among them, this value being nearly equivalent to $d_c=0.4$ g./cc. which appeared in "International Critical Tables", III, p. 248 (1928).

As we know, from van der Waals' b it is possible to calculate the molecular collision diameter, σ, of a gas from the relation:

$$b=4N\frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3, \quad \text{where} \quad N\,(\text{Avogadro's number})=6.025\times10^{23}, \tag{4}$$

but in order to let σ nearly coincide with the molecular collision diameter from viscosity, σ_η, b has usually been taken as

$$b=\frac{RT_c}{8p_c}=\frac{3}{8}\left(\frac{RT_c}{p_cV_c}\right)V_c=b_{corr}. \quad \text{(already denoted)}, \tag{5}$$

which is a solution (the other solution being $b=V_c/3$) obtained from van der Waals' equation and its two derivatives, $(\partial p/\partial V)_T=0$, and $(\partial^2 p/\partial V^2)_T=0$ at the critical point, notwithstanding that the selection of $b_{corr.}$ from these two is merely conventional so far as van der Waals' equation is concerned.

Now, in Landolt-Börnstein, I, Teil 1, p. 369 (1950), there appears $\sigma_\eta=2.27$ A, from which b or otherwise $b_{corr.}$ is calculated to be 14.76 cc./mol., whence $v_c=2.457$ cc./g. or otherwise 1.480 cc./g. The former value is very slightly over the saturation volume, 2.450 cc./g, at 374°C (0.23°C below the critical temperature) observed by Eck and therefore may be acceptable, while the latter is too low and must be rejected.

From complete tests of the author's equation by Henning's tables, p. 25 at 0 to 350°C,

2) W. Ramsay, *Z. phys. Chem.*, **15**, 111 (1894).
3) J. Traube, *Ber.*, **28**, 3292 (1895); ibid., **30**, 273 (1897).
4) E.C. Bingham, L.W. Spooner, *Physics*, **4**, 387 (1933).
5) G.C. Kennedy, *Am. J. Sci.*, **248**, 540 (1950).
6) F.G. Keyes, *J. Chem. Phys.*, **17**, 923 (1949).
7) E. Schroer, *Z. phys. Chem.*, **129**, 79 (1927).
8) H. Eck, *Phys. Z.*, **40**, 3 (1939).

the author has learned that this b value gives better constancy for $(2-\varepsilon)$ than $v_c=2.56$ cc./g. i.e., $b=15.39$ cc./mol. above explained, and so the author, adopting also from Kennedy's data, has carried out calculations for $(2-\varepsilon)$ values and their corresponding percentage deviations, $100\ (p_{calc.}-p_{obs.})/p_{obs.}$, for the pressure range 100 to 1000 bars at 200 to 370°C, and 100 to 2500 bars at 380 to 600°C. A half of their results are tabulated in Tables II and III, and the full values of $(2-\varepsilon)$ are diagrammatically shown in Fig. 1, in which the values from Kennedy's data and the values from Henning's tables are denoted by ○ and × respectively.

It follows from Tables II—III and Fig. 1 that the excellent constancies of $(2-\varepsilon)$ and low percentage deviations throughout the temperature studied afford a conclusive proof to the availability of the author's equation for both liquid and vapour states, and that the linearity of $(2-\varepsilon)$ with temperature is strongly confirmed above 250°C as would be expected, the linearity being expressible by $2-\varepsilon=1.771+0.0001683\ (T-T_c)$ where $T_c=647.4$°K.

At the end of this study we shall add another deduction of the new equation from

TABLE II

$(2-\varepsilon)$ VALUES OF WATER AT 200 TO 600°C

p bars	Temperature in °C										
	200	220	240	260	280	300	320	340	350	360	370
100	1.746	1.748	1.749	1.752	1.754	1.757	(1.745)	(1.756)	(1.763)	(1.768)	(1.774)
150	1.746	1.748	1.750	1.752	1.754	1.758	1.760	1.764	(1.744)	(1.749)	(1.756)
200	1.746	1.748	1.750	1.752	1.755	1.758	1.760	1.764	1.766	1.767	(1.745)
250	1.746	1.748	1.750	1.752	1.755	1.757	1.760	1.764	1.765	1.767	1.769
300	1.746	1.748	1.750	1.753	1.755	1.758	1.761	1.764	1.766	1.767	1.768
350	1.746	1.748	1.751	1.753	1.755	1.758	1.761	1.764	1.766	1.767	1.769
400	1.746	1.748	1.750	1.753	1.755	1.758	1.761	1.764	1.766	1.767	1.769
500	1.745	1.748	1.750	1.753	1.755	1.758	1.761	1.764	1.766	1.768	1.770
600	1.745	1.748	1.750	1.752	1.756	1.758	1.761	1.765	1.766	1.768	1.770
700	1.745	1.747	1.750	1.752	1.755	1.759	1.762	1.765	1.767	1.768	1.770
800	1.745	1.747	1.749	1.752	1.755	1.759	1.762	1.765	1.767	1.769	1.771
900	1.743	1.747	1.749	1.752	1.755	1.758	1.762	1.766	1.767	1.769	1.771
1000	1.743	1.745	1.748	1.752	1.756	1.759	1.762	1.766	1.767	1.769	1.771
mean	1.745	1.748	1.750	1.752	1.755	1.758	1.761	1.765	1.766	1.768	1.770

p bars	Temperature in °C										
	390	410	430	450	470	490	510	530	550	570	590
100	(1.787)	(1.784)	(1.788)	(1.795)	(1.799)	(1.804)	(1.808)	(1.810)	(1.813)	(1.814)	(1.818)
150	(1.767)	(1.776)	(1.784)	(1.791)	(1.798)	(1.805)	(1.812)	(1.816)	(1.820)	(1.822)	(1.826)
200	(1.755)	(1.765)	(1.773)	(1.781)	(1.790)	(1.797)	(1.804)	(1.809)	(1.814)	(1.818)	(1.823)
250	(1.754)	(1.759)	(1.767)	(1.775)	(1.783)	(1.791)	(1.799)	(1.806)	(1.813)	(1.818)	(1.824)
300	1.771	(1.762)	(1.765)	(1.771)	(1.779)	(1.786)	(1.794)	(1.802)	(1.809)	(1.814)	(1.820)
350	1.771	(1.771)	(1.768)	(1.770)	(1.776)	(1.783)	(1.791)	(1.799)	(1.807)	(1.813)	(1.819)
400	1.774	(1.773)	(1.773)	(1.772)	(1.776)	(1.781)	(1.787)	(1.794)	(1.802)	(1.809)	(1.815)
450	1.773	1.776	(1.775)	(1.776)	(1.777)	(1.781)	(1.786)	(1.791)	(1.796)	(1.802)	(1.809)
500	1.773	1.775	1.777	1.778	1.779	1.781	1.786	1.791	1.796	1.801	1.807
600	1.773	1.776	1.778	1.781	1.782	1.784	1.787	1.790	1.795	1.801	1.806
700	1.774	1.777	1.780	1.782	1.784	1.787	1.789	1.792	1.796	1.800	1.804
800	1.774	1.777	1.780	1.783	1.786	1.788	1.791	1.794	1.797	1.801	1.805
900	1.774	1.778	1.780	1.783	1.786	1.789	1.792	1.795	1.798	1.802	1.807
1000	1.774	1.778	1.780	1.783	1.786	1.789	1.792	1.795	1.799	1.803	1.807
1200	1.775	1.778	1.781	1.783	1.786	1.789	1.792	1.795	1.800	1.804	1.808
1400	1.775	1.778	1.780	1.783	1.786	1.789	1.792	1.795	1.799	1.804	1.808
1600	1.775	1.779	1.782	1.786	1.788	1.790	1.793	1.796	1.799	1.803	1.807
1800	1.775	1.779	1.783	1.787	1.790	1.794	1.795	1.797	1.799	1.802	1.806
2000	1.774	1.779	1.784	1.788	1.791	1.794	1.797	1.799	1.801	1.804	1.806
2250	1.774	1.779	1.784	1.788	1.792	1.796	1.799	1.801	1.804	1.806	1.808
2500	1.772	1.778	1.783	1.788	1.792	1.796	1.800	1.803	1.806	1.807	1.810
mean	1.774	1.778	1.781	1.784	1.787	1.790	1.793	1.796	1.799	1.803	1.807

TABLE III

PERCENTAGE DEVIATIONS, 100 $(p_{calc.}-p_{obs.})/p_{obs}$ FOR WATER AT 200 TO 600°C

p bars	Temperature in °C										
	200	220	240	260	280	300	320	340	350	360	370
100	−21.97	+8.29	+7.53	+4.45	+11.47	+11.86	+4.37	+1.91	+0.65	+0.05	+ 0.00
150	−13.15	+3.45	+3.85	+1.76	+ 5.41	+ 7.67	+5.84	+9.51	+9.41	+6.51	+ 4.15
200	−10.59	+2.30	+1.50	−0.88	+ 3.79	+ 5.03	+5.37	+8.37	+3.40	+4.89	+15.95
250	−11.57	+0.66	+1.21	−1.21	+ 1.75	+ 2.89	+3.22	+6.82	+2.87	+5.39	+ 4.74
300	− 5.82	+0.17	+0.45	−1.44	+ 0.69	+ 1.97	+2.05	+5.54	+2.14	+4.71	+ 5.17
350	− 7.50	+1.14	−0.64	−2.95	− 0.65	+ 0.19	+0.83	+4.63	+1.53	+3.80	+ 4.56
400	− 8.94	−0.17	+0.35	−1.43	− 0.08	+ 0.39	−0.02	+3.47	+1.46	+1.85	− 1.66
500	− 2.57	+1.48	+0.22	−1.60	− 0.47	− 0.38	−0.96	+1.73	+0.70	+0.69	+ 1.08
600	− 1.05	+1.84	+0.77	−1.55	− 0.60	− 0.97	−1.36	+1.23	−0.29	+0.09	− 0.58
700	+ 1.19	+2.20	+1.59	−0.80	− 0.90	− 1.08	−1.73	+0.38	−0.97	−0.58	− 0.48
800	+ 2.77	+3.64	+1.63	−0.47	− 0.52	− 1.09	−1.87	−0.13	−0.72	−1.19	− 1.32
900	+ 3.68	+4.52	+2.55	+1.06	− 0.09	− 1.31	−2.15	−0.48	−1.46	−1.59	− 1.75
1000	+ 5.19	+5.17	+3.35	+1.45	+ 0.57	− 1.00	−1.67	−0.44	−1.51	−1.71	− 1.60
mean	7.38	2.69	1.97	1.62	2.08	2.76	2.43	3.43	1.55	2.54	3.31

p bars	Temperature in °C										
	390	410	430	450	470	490	510	530	550	570	590
100	− 1.31	− 0.83	− 0.78	−1.17	−1.56	−1.29	−1.28	−1.10	−0.70	−0.78	−0.67
150	+ 1.58	+ 0.31	− 0.56	−1.09	−1.47	−1.94	−2.12	−2.12	−1.99	−1.75	−1.25
200	+ 7.76	− 4.16	+ 1.99	+0.68	−0.48	−1.15	−1.67	−1.82	−1.86	−1.71	−1.79
250	+18.70	+ 9.27	+ 5.14	+2.61	+1.08	−0.19	−1.20	−1.69	−2.14	−2.11	−2.18
300	+ 7.90	+15.26	+ 9.04	+5.38	+2.80	+1.19	−0.26	−1.26	−1.82	−1.88	−2.01
350	+ 7.34	+11.40	+13.05	+6.34	+4.94	+2.53	−0.67	−0.65	−1.63	−1.93	−2.12
400	+ 4.18	+ 8.98	+10.56	+8.80	+6.28	+3.66	+2.21	+0.72	−0.68	−1.27	−1.67
450	+ 2.60	+ 3.47	+ 7.99	+8.11	+6.68	+4.70	+3.14	+1.86	+0.77	+0.14	−0.52
500	+ 2.12	+ 4.69	+ 5.84	+6.66	+6.30	+5.36	+3.51	+2.17	+1.17	+0.49	−0.01
600	+ 1.45	+ 3.10	+ 3.67	+4.42	+4.55	+4.59	+3.87	+2.89	+1.73	+0.88	+0.36
700	− 0.23	+ 1.77	+ 1.61	+1.94	+2.58	+2.76	+2.88	+2.49	+1.55	+1.33	+0.99
800	+ 0.45	+ 1.20	+ 1.20	+0.83	+1.13	+1.36	+1.47	+1.47	+1.23	+1.00	+0.64
900	+ 0.22	+ 0.65	+ 1.03	+0.84	+0.93	+0.97	+1.06	+0.92	+0.63	+0.39	+0.17
1000	− 0.64	+ 0.40	+ 0.60	+0.80	+0.87	+0.81	+0.89	+0.68	+0.15	−0.08	−0.12
1200	− 1.13	+ 0.17	+ 0.15	+0.71	+0.84	+0.70	+0.64	+0.37	−0.32	−0.54	−0.56
1400	− 0.82	+ 0.06	+ 0.58	+1.02	+1.07	+0.98	+0.94	+0.51	−0.16	−0.66	−0.67
1600	− 0.62	− 0.58	− 1.10	−1.35	−0.99	−0.20	−0.15	+0.27	+0.08	+0.76	+0.01
1800	− 1.53	− 0.86	− 1.51	−1.98	−2.11	−2.72	−1.07	−0.46	−0.14	+0.32	+0.54
2000	− 0.23	− 0.61	− 1.84	−2.54	−2.92	−2.70	−2.34	−1.70	−1.32	−0.29	+0.40
2250	+ 0.04	− 0.48	− 1.89	−2.61	−3.16	−3.23	−3.21	−2.89	−2.68	−1.48	−0.58
2500	+ 1.27	+ 0.28	− 1.07	−2.48	−2.93	−3.35	−3.44	−2.87	−3.14	−2.04	−1.31
mean	2.96	3.26	3.39	2.93	2.65	2.21	1.67	1.47	1.23	1.04	0.88

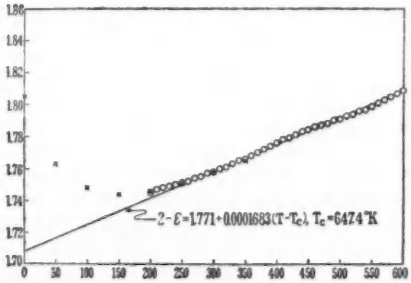

Fig. 1. The temperature dependence of $(2-\varepsilon)$ of water.

the standpoint of kinetic theory of gases by taking the idea of molecular association into consideration in the well-known deduction of van der Waals' equation.[9]

In a liquid, single molecules may form themselves into associated molecules[10], each of which is not a fast-combined molecule but is a group composed of no other molecules than singly existing molecules, or more concretely speaking, into cybotactic groups[11], in

9) e.g., S. Glasstone, "Textbook of Physical Chemistry", p. 289 (2nd Edition).

10) T. Ishikawa, This Bulletin, **4**, 5 (1929); T. Ishikawa, T. Baba, ibid., **11**, 64 (1936).

11) G.W. Stewart, *Rev. Mod. Phys.*, **2**, 116 (1930); *Koll. Z.*, **67**, 130 (1934).

each of which the molecules are arranged in a relatively orderly manner, but the groups are not to be regarded as permanent or as having sharp boundaries, for the movement of the molecules must result in a continual shifting of position and exchange of the members of the cybotactic groups with those in the space between.

If the above idea is extended to the gaseous phase, the force exerted on a single molecule about to strike the wall is, as usually regarded, evidently proportional to the density, ρ, but the number of molecules striking the wall at any instant may be proportional to the density slightly less than ρ, because such molecular groups undoubtedly retard their composition of single molecules striking the wall, that is to say $\rho^{1-\varepsilon}$, if the density under consideration is taken as the simplest power form of ρ, where ε is a correction factor dependent on molecular association and therefore probably independent of pressure, so that the cohesive pressure is proportional to $\rho \cdot \rho^{1-\varepsilon} = \rho^{2-\varepsilon}$. Applying volume correction as is usually done, the author's equation readily follows: $(p+a/V^{2-\varepsilon})(V-b)=RT$, in which constant a is the same as that of van der Waals' equation, if ε is small as compared with unity, and constant b is $V_c/3$ which fits a thermodynamic equality $b=V-R\beta/\alpha$ for normal liquids, hence $a=3p_cV_c^2$, $b=V_c/3$, and $RT_c/p_cV_c=2(1+3V_c^{\varepsilon})/3$; this last relation rejects $b=RT_c/8p_c$ (the other solution of b) for the corrected form of van der Waals' equation.

In conclusion, the author expresses his hearty thanks to Nagasaki American Cultural Center who has furnished him with American journals at his request.

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Reactivity of Coke. III. Effects of Some Metallic Additions on the Surface Area of Cokes from Humic Acid and on the Absolute Reaction Rates of the Coke-Carbon Dioxide System

By Yoshio KAWANA

(Received June 8, 1954)

Introduction

It was recognized long ago that certain metallic impurities as well as added salts played an important role in catalyzing the reaction of carbon with carbon dioxide. Particularly, on the catalytic effects of inorganic additions on the reactivity of coke, a number of works have been written and briefly reviewed by M. A. Mayers.[1] The most effective catalysts to coke or pure graphite among them are the metals of the alkali group, usualy applied as the carbonates as well as the oxides and elemental iron or its carbide. Several other materials have been found to have slight or no effect. Though a great number of work have been published, these effects have hardly been treated quantitatively from the standpoint of chemical reaction rates.

In preceding papers[2,3] we have assumed that the catalytic effects of impurities of coke played an important part in the absolute reaction rates of the coke-carbon dioxide system.

In the present study, we have confirmed quantitatively the effects of some metallic additions on the specific surface area of cokes from humic acid and on the absolute reaction rates of the coke-carbon dioxide system. By the comparison between the cokes prepared from humic acid and metal-humates, the catalytic effects of the metallic constituents of the ash in coke have been examined; sodium, calcium, magnesium, iron and aluminium were used as metals which were most commonly found in the coke ash. The reason why humic acid was selected as the parent carbonaceous material was that the inherent mineral matter in coal might be considered to have partly entered into coal as metal-humates in the initial coalification process[4] and that it might be more important in the consideration of the catalytic

1) M. A. Mayers, "Chemistry of Coal Utilization", Editor, H. H. Lowry, John Wiley and Sons, Inc., New York, Vol. **1**, (1945), p.917.
2) Y. Kawana, This Bulletin, **26**, 507 (1953).
3) Y. Kawana, This Bulletin, **27**, 334 (1954).
4) F. Fisher and W. Fuchs, *Brenn. Chem.*, **8**, 291 (1927). E. Biesalski and Berger, *Braunkohle*, **23**, 197 (1924/25).

effects of the ash in coke than the extraneous mineral matter.

Experimental

Preparation of Humic Acid and Metal-humates.—Humic acid was prepared from Takayama lignite. About 200 g. of dried Takayama lignite, bitumen of which had been previously eliminated by benzene-ethanol azeotropic mixture, was treated with ten-times one per cent sodium hydroxide solution for about five hours at the boiling temperature and after settling during about 15 hours, humic acid was precipitated by a little excess of hydrochloric acid from the upper parts of the solution. The precipitates of humic acid were purified by washing several times with distilled water and then by electrodialysis for about twenty days.

Metal-humates were prepared by treating the humic acid with metal chlorides or carbonate solution by the flow method. About 20 g. of humic acid crushed from 20 to 60 mesh was packed into a glass cylinder and 250 cc. of 1N salt solution passed through the humic acid column at a space velocity of about 0.5 and then the metal-humates were washed by distilled water until chlorine ion disappeared. These metal-humates were dried under reduced pressure. Extra-pure sodium carbonate and metal chlorides were used respectively for sodium-humate and the other metal-humates.

TABLE I
DESCRIPTION OF COKES

Cokes	Density g./cc.	Ash, % dry basis	Composition of ash in coke, %					
			$Na_2O+Na_2CO_3$	$CaCO_3$	MgO	Fe_2O_3	Al_2O_3	SiO_2
H-coke	1.630	2.63	—	1.10	0.55	11.46	31.07	51.15
Na- „	1.625	15.51	84.13	—	—	—	—	—
Ca- „	1.842	7.24	—	45.64	—	—	—	—
Mg- „	1.788	5.60	—	—	20.13	—	—	—
Fe- „	1.835	4.08	—	—	—	39.18	—	—
Al- „	1.862	3.40	—	—	—	—	43.20	—

Preparation of Cokes from Humic Acid and Metal-humates.—The experimental conditions for the preparation of cokes from humic acid and metal-humates were as follows. About 20 g. of humic acid or metal-humates packed in a graphite crucible were put into a silica cylinder and evacuated until about 5 mmHg at room temperature and then carbonized at a heating rate of about 5°C per minute until 1000°C under the reduced pressure of 6—8 mmHg and after maintenance at 1000°C for about one hour, the coke sample was cooled down to room temperature. The cokes carbonized from humic acid, sodium-, calcium-, magnesium-, iron-, and aluminium-humate are defined respectively as H-, Na-, Ca-, Mg-, Fe- and Al-coke.

The analytical results and the densities of coke samples are shown in Table I. All cokes, except for Na-coke treated in high vacuum at lower temperature of 500°C, were subjected to vacuum treatment ($10^{-1}-10^{-3}$ mmHg) at 1100°C for half an hour. H-coke is unfortunately not pure and its ash content is 2.63 per cent. The density and ash contents of metal-cokes are remarkably increased as compared with those of H-coke, and the increase of ash contents of metal-cokes is respectively due to metal ions inserted as metal-humates. The chemical analysis of the ash of metal-cokes was made only on the metal ion inserted.

Apparatus and Procedure.—The apparatus and procedure for determination of the surface area of cokes and for absolute reaction rates of the coke-carbon dioxide system at various temperatures were the same as already described in the first paper.[2] The surface area of cokes was determined by the adsorption of ammonia at 0°C using the B.E.T. method. After that, the reaction of this coke and carbon dioxide at the constant temperature ranging from 730°C to 970°C under constant volume was obtained by measuring the increase in the total pressure of this system against time.

The specific reaction rates per unit area of the coke surface Ka expressed as the number of molecules reacted per sq. cm per second when

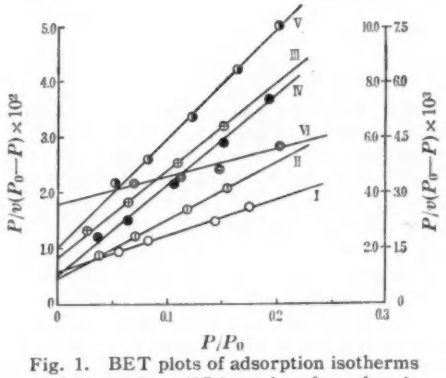

Fig. 1. BET plots of adsorption isotherms of ammonia at 0°C by cokes from humic acid and metal-humates.

	Cokes	Scale
I	H-coke	A
II	Ca-coke	B
III	Mg-coke	„
IV	Fe-coke	C
V	Al-coke	„
VI	Na-coke	A

$P_{co_2}P/_{co}$ was equal to unity, were obtained at various temperatures by the surface area determination together with the reaction rates measurement as already explained in the first paper.

Results and Discussion

Specific Surface Areas of Cokes from Humic Acid and Metal-humates.—The B.E.T. plots of ammonia adsorption at 0°C by cokes from humic acid and metal-humates are shown in Fig. 1 and good straight lines are obtained for a series of relative pressure from about 0.05 to 0.3. According to the usual procedures in the B.E.T. method various values obtained from Fig. 1 are summarized in Table II.

TABLE II

SUMMARY OF SURFACE AREA DATA OF COKES

Cokes	Pre-treatment in vacua °C, hr(mmHg)	Sample weights (g.)	S (m^2)	A (m^2/g.)	A_M/A_H	E_1-E_L (cal./mol.)
H-coke	1100,7 (10^{-4})	0.6306	50.8	80.6	1.00	1295
Na- „	500,2 (10^{-5})	0.3188	53.3	170	2.11	698
Ca- „	1100,1 (5×10^{-3})	0.4262	184.0	433	5.37	1650
Mg- „	1100,1 (10^{-4})	0.2817	100.2	356	4.42	1678
Fe- „	1100,1 (10^{-3})	0.3439	139.4	405	5.02	1900
Al- „	1100,1 (10^{-3})	0.3618	112.0	310	3.84	1660

Before the surface area determination, the coke sample was evacuated at higher temperatures to eliminate the surface oxide and also residual volatile matters; "Pre-treatment in vacua" in Table II shows the conditions of this treatment and the treatment for Na-coke was made at 500°C lest metallic sodium should vaporize by the probable reaction of carbon with sodium oxide.

The specific surface area of metal-coke was about two or five times larger than that of H-coke, and the value of A_M/A_H in Table II is the specific surface area ratio of metal-coke to H-coke. The large specific surface areas of metal-coke compared with H-coke can be expected, as metallic ion exists in highly dispersed state in metal-humate and it is well known that when carbonaceous materials are carbonized with inorganic salts an increase in the surface area is obtained. T.D. Smith[5] had already obtained the similar results with barium mellitate. The values of A_M/A_H must probably depend on not only the valency of the metallic ions, but also their contents in the parent metal-humates.

Absolute Reaction Rates of Cokes from Humic Acid and Metal-humates with Carbon Dioxide.—The reaction rates of the present cokes having the known surface area and carbon dioxide at constant temperature and volume can similarly be expressed by the following equation as already stated in the first paper,

$$dP/dt = KP_{co_2}/P_{co} \qquad (1)$$

where K is a rate constant, P, the total pressure, t, the time, and P_{co_2} and P_{co} denote the partial pressure of carbon dioxide and carbon monoxide respectively.

The specific reaction rates per unit area of the coke surface K_a, expressed as the number of molecules reacted per sq. cm per second at $P_{co_2}/P_{co}=1$, can be calculated by the following equation (Eq. (8) in Ref. (2)) from the rate constant K and the total surface area of the coke S.

$$K_a = a \cdot K \cdot \frac{273}{760} \cdot \frac{1}{60} \cdot \frac{6.02\times10^{23}}{22400} \cdot \frac{1}{S\cdot10^4} \qquad (2)$$

The relations between K_a and $1/T$ for various cokes are shown in Fig. 2 and K_a may be expressed as:

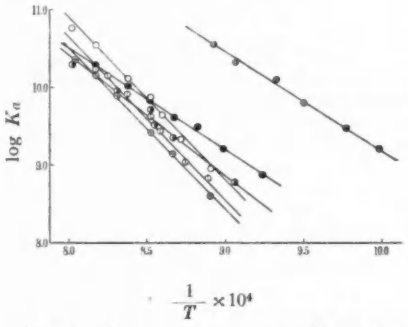

Fig. 2. Relations between log K_a and $1/T$
○ H-Coke, ⊕ Mg-Coke ◑ Al-Coke
◐ Ca-Coke, ● Fe-Coke ◎ Na-Coke

$$K_a = A \exp.(-E/RT), \qquad (3)$$

where A is a constant and E, the experimental activation energy. The values of A and E determined by the least squares are summarized in Table III. Although the large difference in A and E among H-, Ca- and

5) T. D. Smith, *J. Chem. Soc.*, **1952**, 923.

TABLE III

THE VALUES OF A AND THE ACTIVATION ENERGIES E

Cokes	$A_{obs.}$ molecules (cm^{-2} sec^{-1})	$A_{calcd.}$ molecules (cm^{-2} sec^{-1})	E (kcal./mol.)
H-coke	4.46×10^{27}	5.57×10^{27} (1173°K)	96.0
Na- „	7.75×10^{21}	4.98×10^{27} (1050°K)	58.3
Ca- „	1.12×10^{27}	5.57×10^{27} (1173°K)	94.0
Mg- „	1.29×10^{27}	„	95.1
Fe- „	1.00×10^{21}	„	60.1
Al- „	8.91×10^{22}	„	71.8

Mg-coke can not be seen, those of Fe-, Al- and Na-coke are much smaller than H-coke.

Provided that the reaction mechanism presented in the first paper may be applicable, the quantity A must be calculated from the following equation applying the absolute reaction rates theory (Eq. (14) in Ref. (2)),

$$A=kT/h\cdot L\cdot f_{co}/f_{co_2}\cdot f_a^*/f_s \qquad (4)$$

The calculated values of A are also given in Table III, using $L=10^{15}$, $f_a^*/f_s=1$, $T=1050$°K for Na-coke and $T=1173$°K for the other cokes. The difference between the observed and calculated values for H-, Ca- and Mg-coke is very small, but for Fe-, Al- and Na-coke, it is much greater than expected from the theory. Accordingly, it is concluded that the simple reaction mechanism presented in the first paper may be applicable for H-, Ca- and Mg-coke, but for the other cokes, a more complicated reaction may probably be occurring.

The specific reaction rates per unit area of the coke surface, K_{aM} for metal-cokes and K_{aH} for H-coke at various temperatures, can be calculated from Eq. (3) using the experimental values of A and E, and the ratio, K_{aM}/K_{aH}, is given in Table IV. From these values of K_{aM}/K_{aH}, we can clearly see the effects of metallic impurities on the absolute reaction rates of the coke-carbon dioxide system.

These values for Na-, and Fe-coke at lower temperatures are of the order of 10^1 or 10^2 and under the present experimental conditions it may be considered that metallic sodium for Na-coke and metallic iron or its carbide for Fe-coke would most probably take part in the reaction. These results agree well with those of earlier[1] and recent studies[5] that the most effective catalysts of inorganic additions to coke or pure graphite are the metals of the alkali group and metallic iron or its carbide.

In Ca-, and Mg-coke, calcium and magnesium impurities would exist as the oxides, which intend to inhibit the specific reaction rates per unit surface area to cabron dioxide as seen in Fig. 2 and Table IV. The behavior of Al-coke resembles very much to that of Fe-coke. The ratio of the maximum value of K_a to the minimum at one temperature for various cokes is in the range from 1.74×10^1 at 1000°C to 1.10×10^3 at 700°C evaluated from Table IV. It was already stated that these ratios were about 16 or 20 for various cokes investigated in the first paper and that K_a at 950°C in the second paper[3] changed irregularly with these ratios of 10^1 or 10^2 by the heat treatment of cokes from 1000° to 2000°C, and these experimental facts have been considered as the catalytic effects of the ash in coke. The present results of strong effects of metallic impurities would confirm that these considerations might be most reasonable.

Metallic impurities introduced as metal-humates have strong effects on the specific surface area of cokes from humic acid and on the absolute reaction rates of the coke with carbon dioxide, and the products of A_M/A_H in Table II and K_{aM}/K_{aH} in Table IV represent the effects of metal impurities on the apparent or relative reactivity of the coke. These values of the product are in the range from 1.08 to 1.01×10^4 for all metallic impurities investigated at 700° to 1000°C. That is, all metallic impurities investigated

6) E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.*, **44** 1048 (1952); W. F. K. Wynne-Jones, H. E. Blayden and H. Marsh, *Brenn. Chem.*, **33**, 238 (1952).

TABLE IV

THE RATIOS OF THE SPECIFIC REACTION RATES OF METAL-COKES TO THAT OF H-COKE AT VARIOUS TEMPERATURES

Cokes	K_{aM}/K_{aH}			
	700°C	800°C	900°C	1000°C
H-coke	1	1	1	1
Na- „	4.78×10^2	7.75×10^1	1.74×10^1	4.89
Ca- „	8.7×10^{-1}	7.9×10^{-1}	7.4×10^{-1}	6.9×10^{-1}
Mg- „	4.36×10^{-1}	4.26×10^{-1}	4.07×10^{-1}	3.98×10^{-1}
Fe- „	2.45×10^1	4.36	1.05	3.09×10^{-1}
Al- „	5.36	1.66	6.30×10^{-1}	2.81×10^{-1}

in the present study increase the relative reactivity of the coke.

Summary

The surface area of cokes from humic acid and metal-humates and the absolute reaction rates of these cokes to carbon dioxide at various temperatures have been determined by the same method and procedure as those described in the first paper.

The specific surface area of cokes from metal-humates are about two or five times larger than the coke from humic acid, and this increase is expected from the well-known fact that when carbonaceous materials are carbonized with inorganic salt an increase in the surface area is obtained.

The specific reaction rates per unit surface area K_a of these cokes and carbon dioxide can be expressed by an equation

$$K_a = A \exp.(-E/RT),$$

and the values of A and activation energies E have been determined. The activation energies of cokes from humic acid, Ca- and Mg-humates are about 95 kcal./mol. and a large difference is not seen among them, but those of cokes from Fe-, Al- and Na-humates are about 25–40 kcal./mol. smaller than H-coke. The experimental values of A for cokes from humic acid, Ca- and Mg-humate are in satisfactory agreement with those expected from the application of the absolute reaction rates theory to the reaction mechanism already presented in the first paper, but those of A for cokes from Fe-, Al- and Na-humate are much smaller than expected from the theory. These results may be considered to indicate that the more complicated reaction must be occurring for cokes from Fe-, Al- and Na-humates. Calcium and magnesium impurities have effects of decreasing the specific reaction rates per unit surface area of the coke from humic acid to carbon dioxide and on the other hand, aluminium, especially iron and sodium impurities at lower temperatures have great effects of increasing the specific reaction rates. The effects of these sodium and iron impurities agree well with the earlier results and the present results also confirm that the catalytic effects of impurities in coke play an important role in the absolute reaction rates of the coke-carbon dioxide system, which was assumed in previous papers.

By considering the effects of metallic impurities on both the specific surface area of cokes from humic acid and the specific reaction rates per unit surface area of the coke with carbon dioxide, all metallic impurities investigated increase the relative reactivity of the coke from humic acid and for example, sodium impurities increase the apparent reactivity of the coke about 10^3 times at 700°C.

In conclusion, the author wishes to express his heart-felt gratitude to Mr. A. Baba, Dr. H. Honda and Mr. Y. Yoshida for their valuable suggestions and deep interest in this study. The author's thanks are also due to Mr. R. Sato for his kind assistance, Mr. T. Yamakawa for a gift of humic acid and Mr. Y. Hirose for chemical analysis of the ash in coke.

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On the Thermal Dissociation of Organic Compounds. VI. The Effect of the Substituent and That of the Solvent on the Thermal Dissociation of Ureas

By Teruaki MUKAIYAMA[1], Shōichiro OZAKI and Toshio HOSHINO

(Received June 9, 1954)

Introduction

It is known that, on heating, ureas dissociate thermally into isocyanates and amines.

$$RHN-CO-NHR \rightleftarrows R-N=C=O+H_2N-R$$

The kinetics of the thermal dissociation of urea and some substituted ureas in fatty acid solvents have been studied[2-4] and, in the case of urea in *n*-butyric acid, for example, the mechanism shown by Equations (1)-(4) was suggested.

1) Department of Physics and Chemistry, Gakushuin University, Mejiro, Tokyo.
2) T. Hoshino, T. Mukaiyama and H. Hoshino, *J. Am. Chem. Soc.*, **74**, 3097 (1952).
3) T. Hoshino, T. Mukaiyama and H. Hoshino, This Bulletin, **25**, 392 (1952).
4) T. Mukaiyama and T. Matsunaga, *J. Am. Chem. Soc.*, **75**, 6209 (1953).

$$H_2N-CO-NH_2 \rightleftarrows H-N=C=O+NH_3 \quad (1)$$
$$H-N=C=O+C_3H_7COOH \rightleftarrows C_3H_7CO-O-CONH_2 \quad (2)$$
$$C_3H_7CO-O-CONH_2 \longrightarrow C_3H_7CO-NH_2+CO_2 \quad (3)$$
$$NH_3+C_3H_7COOH \rightleftarrows C_3H_7COONH_4 \quad (4)$$

The dissociation of urea in fatty acid was considered as a general acid catalyzed reaction, which is shown by the following process.

$$H_2NCONH_2+RCOOH \longrightarrow H_3\overset{+}{N}CONH_2+RCOO^- \quad (5)$$
$$H-N=C=O \longleftarrow H_2N-\underset{\displaystyle -H^+}{\overset{\displaystyle +}{C}}=O+NH_3$$

As shown in the previous reports, the rates of dissociation of ureas are deeply dependent on the nature of solvents and the kind of substituents. In the present work, the dissociation of eight substituted ureas in five fatty acids were studied and the relation between the nature of acids and the kind of substituents were discussed.

The reaction can be followed by measuring the rate of evolution of carbon dioxide (Eq. 3), provided it is evolved as soon as formed. Since the reaction temperature was near 155° it is reasonable to believe that this is true, and also that the reverse reaction is negligible under the conditions of the experiments. If reaction (1) is the rate-determining step, then the rate of dissociation is measurable.

On plotting the logarithm of volume of carbon dioxide, ΔY, evolved at regular intervals of time, we have obtained a straight line. This indicates a first order reaction rate. The rate constant is given by the gradient of such a plot,[5] as shown in Fig. 1.

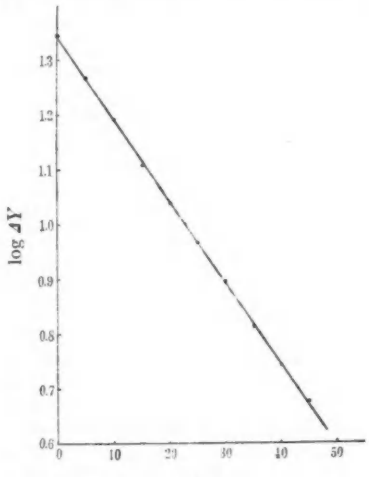


Fig. 1. The plot of t against log ΔY. 1, 1, 3-Triethylurea in n-capric acid at 155.1°C.

Experimental

The apparatus employed was the same as that described in previous reports.[2,3] In this experiment, the reaction vessel was maintained at desired, constant temperature by immersion into the thermostat containing rape-seed oil. In order to prevent the heat loss at this high temperature, the thermostat was surrounded by asbestos and placed in a cabinet thickly filled with glasswool. The temperature control of the reaction thermostat was accurate to ±0.03 within the temperature range 140—160° using a tetraline-mercury regulator.

Preparation of Materials.—*1, 1-Dimethylurea*: the commercial product, m.p. 181°, was used. *1, 3-Diethylurea*: from ethyl isocianate[6] and water, m.p. 110°, recrystallized from petroleum ether. *1, 1, 3-Triethylurea*[7]: from ethyl isocyanate and diethylamine, m.p. 65°, recrystallized from petroleum ether. *1, 3-Diisopropylurea*: from isopropyl isocyanate[8] and water, m.p. 190°, recrystallized from 70% aqueous ethanol. *1, 3-Dihexylurea*: from hexyl isocyanate and water, m.p. 75°, recrystallized from petroleum ether. Found N, 12.79%. Calcd for $C_{13}H_{28}N_2O$: N, 12.28%. *Hexyl isocyanate* was prepared from heptoic acid hydrazide *via* heptoic acidazide by heating in anhydrous benzene, b.p. 71—72°/31 mm. *1, 3-Dibenzylurea*: from benzyl isocyanate[9] and water, m.p. 167°, recrystallized from ethanol. *1, 1-Diethyl-3-isopropylurea*: from isopropyl isocyanate and diethylamine, m.p. 66°, recrystallized from petroleum ether. *1, 3-Di-t-butylurea*: from urea and *t*-butyl alcohol by the method described in Organic Syntheses,[10] m.p. 243° (in sealed tube), recrystallized from 80% aqueous ethanol.

Solvent: n-Butyric and n-caproic acids were distilled after boiling with phosphorous pentoxide and re-distilled employing a fractionating column, b.p. 159–160° and 104–106°/16.5–17mm, respectively. n-Capric acid was twice distilled in vacuo b.p. 121–123°/3.2–3.5 mm. Phenylacetic acid was recrystallized from water and then distilled in vacuo b.p. 117°/4.5 mm. Benzoic acid was used without further purification, m.p. 122°.

The rate constants for the thermal dissociation of ureas were determined under the following conditions: 1, 1, 3-triethylurea (1 mole) in n-capric acid (50 moles), given as an example of a typical run: Fig. 1. Ureas (1 mol.) in a carboxylic acids (50 mol.). The ureas were 1, 1-dimethyl, 1, 3-diethyl, 1, 1, 3-triethyl, 1, 3-diisopropyl, 1, 3-dihexyl, 1, 3-dibenzyl, 1, 1-diethyl-3-isopropyl and 1, 3-di-*t*-butyl. The acids were n-butyric, n-caproic, n-capric, phenylacetic and benzoic.

The results are summarized in Table I. The rates were first order with respect to ureas.

5) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).
6) T. Curtius and H. Hille, *J. prakt. Chem.*, **64** 401 (1901).
7) Wurtz, Beilstein, IV, 120.
8) O. Hambsch, *J. prakt. Chem.*, **125**, 182 (1930).
9) T. Curtius and E. Boetzlen, *J. prakt. Chem.*, **64**, 316 (1901).
10) "Organic Syntheses," **29**, 18.

TABLE I

THE RATE CONSTANTS OF THE THERMAL DISSOCIATION OF UREAS IN FATTY ACIDS

$k \times 10^2$ (min.$^{-1}$) (at t°C)

ureas \ acids	*n*-butyric acid	*n*-caproic acid	*n*-capric acid	phenylacetic acid	benzoic acid
1, 1-dimethylurea	1.11 (139.5°)	2.97 (155.2°)	1.2 (155.1°)	3.02 (155.0°)	0.545 (155.0°)
1, 3-diethylurea		2.65 (155.2°)	2.66 (155.1°)	2.86 (155.0°)	1.07 (155.0°)
1, 1, 3-triethylurea	4.09 (139.5°)	3.42 (155.0°)	3.39 (155.1°)	10.9 (155.0°)	2.09 (155.0°)
1, 3-diisopropylurea	1.79 (139.6°)	2.61 (155.0°)	3.08 (155.0°)	4.86 (155.0°)	0.967 (154.95°)
1, 3-dihexylurea	1.24 (139.6°)	3.65 (155.0°)	3.26 (155.0°)	2.10 (154.9°)	0.659 (155.0°)
1, 3-dibenzylurea	1.27 (139.6°)	2.68 (155.0°)	2.70 (155.0°)	3.85 (154.9°)	0.418 (155.0°)
1, 1-diethyl-3-isopropylurea	3.15 (139.45°)	6.2 (155.0°)	3.19 (155.0°)	very fast (154.9°)	1.60 (155.1°)
1, 3-di-*t*-butylurea	3.87 (139.4°)	3.93 (155.0°)	6.8 (155.0°)	fast (155.0°)	0.900 (154.95°)

Discussion

According to the results of experiments summarized in Table I, the effects of solvents on the rate of dissociation of ureas are in the following order:

phenylacetic acid, *n*-butyric acid>*n*-caproic acid, *n*-capric acid>benzoic acid.

The *pKa* values for these five acids are shown in Table II.

TABLE II

THE *pKa* VALUES FOR FATTY ACIDS[11]

acid	*pKa*
n-butyric acid	4.82
n-caproic acid	4.85
n-capric acid	4.90
phenylacetic acid	4.31
benzoic acid	4.17

As known from their *pKa* values, if the dissociation of urea proceeds according to a general acid catalyzed reaction (5), the effects of solvents on the rate of dissociation should fall in the order,

Benzoic acid>phenylacetic acid>*n*-butyric acid>*n*-caproic acid>*n*-capric acid.

Benzoic acid, as shown in the above order, should accelerate the rates of dissociation of ureas more than the other four acids. However, the rates of dissociation of ureas in benzoic acid are very slow in comparison with that in other acids and this shows that the previously proposed mechanism (5) is an unsatisfactory one to explain the dissociation reaction.

As to the effects of substituents, it is shown by the present experiment that the rate of dissociation increases in the series,

urea<1, 1-dimethylurea≤1, 3-dibenzylurea <1, 3-dihexylurea≤1, 3-diethylurea, 1, 3-diisopropylurea<1, 3-di-*t*-butylurea≤1, 1, 3-triethylurea, 1, 1-diethyl-3-isopropylurea.

In the process of dissociation of urea, the one nitrogen atom of urea accepts a proton to form an amine and the other nitrogen atom donates a proton to form an isocyanate. Thus, there are two factors which can be considered to dominate the dissociation of ureas.

(a) Ability of one nitrogen atom in urea as a proton-acceptor, namely basicity.

(b) Ability of one nitrogen atom in urea as a proton-donor, namely acidity.

When one compares the relative strength of basities of ureas, those of corresponding amines may be used. A urea nitrogen atom having two substituents is bonded to three carbon atoms and therefore might be expected to behave as a tertiary one. However, by comparing the rate of dissociation of 1, 1, 3-triethylurea with that of 1, 3-diethylurea, the former urea dissociates more easily than the latter. The one nitrogen atom of these two ureas has the same substituent group and therefore the difference in reactivity is due to the difference in the ability of the other nitrogen atom as a protonacceptor. The fact shows that 1, 1, 3-triethylurea has a stronger tendency to accept a proton than 1, 3-diethylurea, namely, the former urea might be more basic. This conclusion does not agree with the consideration that the relative basity of a urea nitrogen atom having two substituents corresponds to that of a tertiary amine. In considering the structure of 1, 1, 3-triethylurea, one of three carbon atoms bonded to a urea nitrogen is that of carbonyl and, be-

11) L. F. Fieser and M. Fieser "Text-book of Organic Chemistry" p. 157 (1952).

cause of the planar configuration of carbonyl group, the B-strain[12] considered to exist in an ordinary tertiary amine is reduced in the urea. Accordingly, it may be reasonable to assume that the relative strength of a urea nitrogen atom having two substituents corresponds to the basity of secondary amine and that of a urea nitrogen having one substituent corresponds to that of primary amine.

The *pKb*[13] values for the corresponding amines are shown in Table III.

TABLE III
THE *pKb* VALUES FOR AMINES[13]

amine	*pKb*
dimethylamine	3.22
trimethylamine	4.13
ethylamine	3.28
diethylamine	2.90
triethylamine	3.36
isopropylamine	3.28
t-butylamine	3.47
benzylamine	4.62
ammonia	4.75

Just as the protonation of urea molecule by the solvent acid is an important factor on the dissociation, the deprotonation of urea molecule by the solvent acid is also an important one. In 1, 3-dibenzylurea, one nitrogen atom is a weak base which facilitates the deproponation and hence the reaction.

The effects of solvents and those of substituents mentioned above are explained by considering the following mechanism.

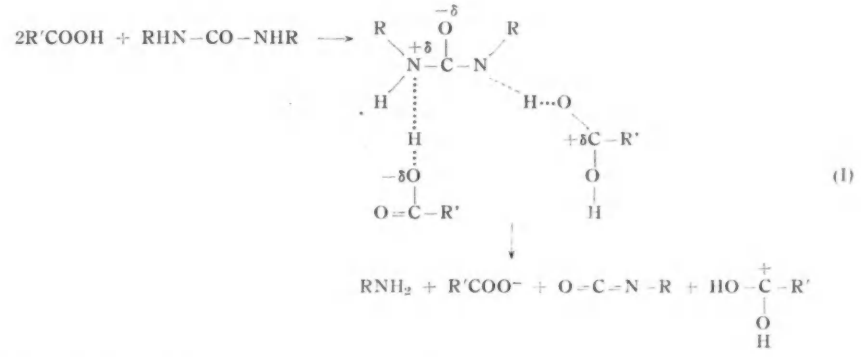
Under the condition of the experiments, the molar ratio of fatty acid to urea is 50 : 1, therefore the transition state (I) which contains two fatty acid molecules and one urea molecule might be considered as a reasonable one. One acid in the state (I) acts as an acid to donate a proton and the other acts as a base to accept a proton.

Contrary to the expectation that the stronger the acidity of solvent acid the faster the dissociation, the rates of dissociation of ureas in benzoic acid are slower than in the other acids. This slow rate may come from the fact that the weak basicity of benzoic acid makes the deprotonation of urea in state (I) more difficult. That the rates of dissociation of ureas in *n*-butyric acid are faster than those in *n*-caproic and *n*-capric acids will be explained by considering the difficulty of forming a state (I) in the latter acids because of their spatial requirement. As described in the previous report,[2,4] the rates of dissociation of ureas in acetic, propionic and *n*-butyric acids fall in the following order:

acetic acid > propionic acid > *n*-butyric acid.

This order agrees with the above consideration that the smaller the molecular size the greater the frequency to attack urea molecule.

The effects of substituents controlled by two factors (a) and (b) on the thermal dissociation of ureas can also be explained by considering the state (I), in which two acids



The effect of factor (a) on the dissociation reaction is shown in the results that 1, 1-diethyl substituted ureas dissociate faster than other 1-monosubstituted ureas and that urea itself dissociates slower than other substituted ureas. However, the results that the rate of dissociation of 1, 3-dibenzylurea is nearly equal to that of 1, 3-dihexylurea and that 1, 3-di-*t*-butylurea dissociates more readily than 1, 3-diethylurea can not be explained by the factor (a) alone. And factor (b), i.e. the ability of one nitrogen atom in urea as a proton-donor comes into consideration.

12) In general, secondary amine is a stronger base than a tertiary one. This phenomenon does not agree with the tendency anticipated from the palar effect, and this was explained by the so-called B-strain proposed by H. C. Brown, L. N. Ferguson, "Electron Structures of Organic Molecules" p. 114, (1952).

13) Calculated from the dissociation constants. I. Heilbron et al., "Dictionary of Organic Compounds," Eyre & Spottiswoode Pub. Ltd. London (1946).

act as a proton-acceptor and as a proton-donor to one urea molecule at the same time.

It can be concluded that the thermal dissociation of ureas in fatty acids is more favorable when solvent acids and substituents tend to donate or accept a proton.

Summary

The rate constants of the thermal dissociation of 1,1-dimethyl, 1,3-diethyl, 1,3-diisopropyl, 1,1,3-triethyl, 1,3-dihexyl, 1,3-dibenzyl, 1,1-diethyl-3-isopropyl and 1,3-di-*t*-butyl ureas in *n*-butyric, *n*-caproic, *n*-capric, phenylacetic and benzoic acids were determined. The effects of substituents and those of solvents on the reaction rate were discussed. The transition state of the dissociation containing two fatty acids and one urea molecule was considered and the experimental results were reasonably explained by the proposed mechanism.

The Authors express their hearty thanks to Mr J. Kanai for his help in the early stage of this experiment.

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Alkylalkoxypolysiloxanes. II. Ethylisopropoxypolysiloxanes

By Rokuro ŌKAWARA and Iwao ISHIMARU

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The reaction of secondary alcohol and chlorosilanes has not been so well studied as that of primary alcohol and chlorosilanes. Recently we reported on the preparation of isopropoxypolysiloxanes[1] from isopropanol and corresponding chloropolysiloxanes with good yield. The reaction of isopropanol and diethyldichlorosilane in refluxing benzene was studied by McCusker and Green.[2]

Now we wish to report on the preparation and properties of ethylisopropoxydichlorosilane (I), ethyldiisopropoxychlorosilane (II) and ethylisopropoxypolysiloxanes including ethyltriisopropoxysilane (III). Ethylisopropoxychlorosilanes, i. e. (I) and (II), were prepared by partial isopropanolysis of ethyltrichlorosilane. Data on these materials are given in Table I. In the case of preparing ethylethoxypolysiloxanes[3], in which one ethyl group attaches to each silicon atom, ethylethoxychlorosilane and ethyltriethoxysilane were mixed in various mole ratios and refluxed. In this experiment, the ethylisopropoxypolysiloxanes having the similar structure were prepared by the same method. But in this case the mixture of ethyltrichlorosilane (1 mol.) and isopropanol in a different mole ratio (2.3 to 2.5 mol.) were refluxed. The chlorine content of the refluxing mixture was gradually decreased by a thermal reaction and there was obtained some amount of isopropylchloride in a cold trap. It may be supposed that the thermal reaction occurred at the refluxing temperature between Si-Cl and $Si\text{-}OC_3H_7$ with the result of the formation of siloxane bond and isopropylchloride as follows:

$$Si\text{-}OC_3H_7 + Si\text{-}Cl = Si\text{-}O\text{-}Si + C_3H_7Cl. \qquad (1)$$

By fractional distillation, the chlorine-free mixture was separated into monomer, dimer and trimer fractions. By a rigorous redistillation of the polymer fractions, a small amount of cyclotrimer was obtained between the plateaus of dimer and linear trimer. Data on these polysiloxanes which belong to the linear-and cyclo-series as indicated by formula (A) and (B) are given in Table III.

$$RO\left[\begin{array}{c} C_2H_5 \\ | \\ SiO \\ | \\ OR \end{array}\right]_n R \qquad (A)$$

$R=CH(CH_3)_2$ $n=1-3$

$$\left[\begin{array}{c} C_2H_5 \\ | \\ SiO \\ | \\ OR \end{array}\right]_n \qquad (B)$$

$R=CH(CH_3)_2$ $n=3$

To obtain a series of compounds as indicated by formula (C) which have more isopropoxy groups in a molecule than the compounds of formula (A) have, the thermal reaction between (II) and tetraisopropoxysilane (IV) or (II)

1) R. Okawara, T. Tanaka and I. Ishimaru, This Bulletin, **27**, 45 (1954).
2) P. A. McCusker and C. E. Green, *J. Am. Chem. Soc.*, **70**, 2807 (1948).
3) R. Ōkawara, This Bulletin, **27**, 428 (1954).

$$C_2H_5\left[\begin{array}{c}OR\\|\\SiO\\|\\OR\end{array}\right]_n R \qquad (C)$$

$R=CH(CH_3)_2$ $n=2-3$

and hexaisopropoxydisiloxane (V) was carried out.

On fractional distillation of the chlorine-free product, the constant boiling fraction which belongs to the series (C) was obtained. But there is a probability of the compound of the series (C) being contaminated by a small amount of the compound of series (A) or the isopropoxypolysiloxane of the same polymer size which may be formed by side reactions.

Experimental

Starting Materials.—The ethyltrichlorosilane used in this experiment was prepared by the reaction of ethylchloride with copper-silicon and was purified by fractionation through a helices-packed column of about 20 plates. The redistilled fraction having the boiling point 98°–99°C (760mm Hg) was taken as a starting material. Found: Cl, 64.0. Calcd. for $C_2H_5SiCl_3$: Cl, 65.0%.

Exp. No.	Ethyltrichlorosilane (a) (g.)	Isopropanol (b) (g.)	Mole Ratio (b)/(a)
1	29.5	27	2.5
2	45.5	40	2.4
3	49	42	2.34

Isopropanol of Shell Chemicals (b.p. 82.2°C, n_D^{20} 1.3776) was used without further purification. Tetraisopropoxysilane (IV) and hexaisopropoxydisiloxane (V) used for the preparation of the compounds of the series (C) were prepared as already described.[1]

Tetraisopropoxysilane (IV): b.p. 93°–4°C/28 mmHg, n_D^{20}1.3835, d_4^{20}0.8744. Found: Si, 10.59, Calcd. for $(C_3H_7O)_4Si$: Si, 10.62%.

Hexaisopropoxydisiloxane (V): b.p. 82°–3°C/1mmHg, n_D^{20}1.3921, d_4^{20}0.9236. Found: Si, 13.14, Calcd. for $(C_3H_7O)_3Si_2O$: Si, 13.17%.

Preparation of Ethylisopropoxychlorosilanes.—*Ethyldiisopropoxychlorosilane (II).* Ethyltrichlorosilane (41g.: 0.25 mol.) was placed in a 500 cc. three-necked flask equipped with an efficient stirrer, a reflux condenser and a dropping funnel. Isopropanol (30g.: 0.5 mol.) was added drop by drop for one hour with vigorous stirring. During the addition the temperature of the mixture was kept at 3° to 5°C. After the addition the mixture was aerated at room temperature (10°C) with dry air to bubble off the hydrogen chloride until the weight of the mixture attained the calculated value. After aerating for 40 minutes the weight of the mixture attained the calculated value (53g.) and the chlorine content of the mixture was 16.6% (calcd. 16.8%). The mixture was fractionated through a semi-micro stedman column of about 20 plates under reduced pressure.

The following fractions were obtained.

The first fraction: 4g., b.p. 70°–76°C/48 mmHg.

"Refluxing Mixture"		% Cl	
(g.)	(% theory)	Found	Calcd.
41	102	7.9	8.0
61	100	9.8	9.7
65	100	10.3	10.8

Found Cl, 18.1%.

The second fraction: 27g., b.p. 76°C/48 mmHg. Found Cl, 16.7%.

The third fraction: 4g., b.p. 76°–78°C/48 mmHg. Found Cl, 13.6%.

The residue: 11g. Found: Cl, 2.1%.

The second fraction (yield: 50% theory) may be considered to be pure (II). (Calcd. for (II): Cl, 16.8%).

Ethylisopropoxydichlorosilane (I). From 41g. (0.25 mol.) of ethyltrichlorosilane and 15g. (0.25 mol.) of isopropanol treated in the same way as above, 44g. of the product (calcd. 47g.) of which the chlorine content is 36% (calcd. 37.9%) was obtained. By fractionating the product through the same semi-micro stedman column under 60 mmHg, 15g. of the fraction boiling at 67°C/60 mmHg was collected. Found Cl, 37.4 Calcd. for (I): Cl, 37.9%. The constants of ethylisopropoxychlorosilanes were determined by the redistilled product and are summarized in Table I.

TABLE I

ETHYLISOPROPOXYCHLOROSILANES

Name	Boiling Point °C/mmHg	Refractive Index $n_D^{2,3}$	Density d_4^{20}	Molecular Refraction Found (Calcd.)*	% Cl Found (Calcd.)
Ethylisopropoxydichlorosilane (I)	66–7/59	1.4115	1.0508	44.23 (44.19)	37.4 (37.9)
Ethyldiisopropoxychlorosilane (II)	74–6/48	1.4018	0.9361	54.73 (54.58)	16.7 (16.8)

* Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

Preparation of the Ethylisopropoxypolysiloxanes of the Series (A) and (B); (Exp. 1 to 3 in Table II).—The "refluxing mixtures" of Exp. 1 to 3 were prepared by adding isopropanol to ethyltrichlorosilane with vigorous stirring and aerating the products at room temperature until the weight of the products attained the calculated value as described in the preparation of ethylisopropoxychlorosilanes. The amounts of the ethyltrichlorosilane, isopropanol and the product obtained were as follows.

The composition of the product which was used as the "refluxing mixture" was calculated from its chlorine content by assuming that only (II) and (III) were present in it and was given in Table II as "Refluxing Mixture".

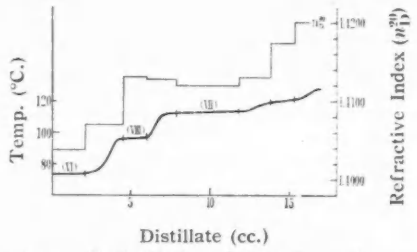

Fig. 1. Redistillation of the polymer fraction of ethylisopropoxypolysiloxanes. (VI): Dimer, (VII): Linear trimer, (VIII): Cyclotrimer

TABLE II

Exp. No.	Refluxing Mixture Compds.* (A) (B)	(g.)	Mole Ratio (A)/(B)	Time (hr.)	Highest Temp. (°C)	Product (g.)	Product % theory**	Composition of the product Monomer (%)	Dimer (%)	Trimer (%)	Residue (%)
1	(II)	18.8	1	64	205	29	87.8	60	12	—	28
	(III)	21.2									
2	(II)	35.5	1.5	64	205	43	91.5	47	8	13	32
	(III)	25.5									
3	(II)	41.4	2	112	205	47	96	31	14	7	48
	(III)	23.6									
4	(II)	4.5	0.5	144	210	9.8	86	12	11	—	77
	(IV)	8.6									
5	(II)	10.5	1	64	285	24.9	88.6	0	36	20	44
	(V)	21.4									

* (II): $C_2H_5Si(OC_3H_7)_2Cl$, (III): $C_2H_5Si(OC_3H_7)_3$
(IV): $(C_3H_7O)_4Si$, (V): $(C_3H_7O)_3Si_2O$

** Ratio of the amount of the polysiloxane obtained to the calculated amount of the polysiloxane.

TABLE III

ETHYLISOPROPOXYPOLYSILOXANES

Polymer Size	Name	Boiling Point °C/mmHg	Density d_4^{20}	Refractive Index n_D^{20}	Molecular Refraction Found (Calcd.)*	Molecular Weight Found** (Calcd.)	% Si Found (Calcd.)
	Series (A) and (B)						
Monomer	Triisopropoxyethylsilane (III)	65.4/8	0.8607	1.3938	65.12 (64.97)	241 (234)	11.84 (11.98)
Dimer	Tetraisopropoxy-1,3-diethyldisiloxane (VI)	73/0.8	0.9091	1.4038	98.58 (98.26)	362 (367)	15.64 (15.32)
Linear Trimer	Pentaisopropoxy-1,3,5-triethyltrisiloxane (VII)	112–3/0.8	0.9444	1.4120	131.38 (131.55)	489 (499)	17.14 (16.88)
Cyclotrimer	Triisopropoxy-1,3,5-triethylcyclotrisiloxane (VIII)	96–7/0.8	—	1.4131	—	398 (397)	20.75 (21.23)
	Series (C)						
Dimer	Pentaisopropoxy-ethyldisiloxane (IX)	82–3/0.8	0.9193	1.3962	103.71 (103.65)	404 (397)	13.67 (14.15)
Trimer	Heptaisopropoxy-1-ethyltrisiloxane (X)	114–5/0.8	0.9570	1.4027	141.9 (142.3)	563 (559)	15.21 (15.06)

* Calculated from bond refractivities (Table I footnote)

** Cryoscopic measurements in benzene

The mixture was refluxed until the chlorine could not be detected by Beilstein test. During the course of refluxing a small amount of liquid product was collected in a cold trap. Its boiling point (34.5°C) accorded well with that of isopropylchloride. The time required to produce the chlorine-free mixture and the highest refluxing temperature attained are cited in Table II.

The products were fractionated through a semimicro stedman column of about 30 theoretical plates under reduced pressure. Ethyltriisopropoxysilane (III) was distilled out at 65°C/8 mmHg. The disiloxane and trisiloxane fractions were the succeeding plateaus which were obtained at 73°C/0.8 mmHg and 112°C/0.8 mmHg. The amounts in percentage of these plateaus including the intermediate fractions cut on the distillation curve are also shown in Table II. As the amounts of disiloxane and trisiloxane fractions were small and fairly large amounts of the intermediate fraction was found between them, all the polysiloxane fractions were again fractionated rigorously through the same column. The distillation curve and the refractive index of the small portions are shown in Fig. 1.

Properties of these compounds are given in Table III.

In the preparation of ethylethoxypolysiloxanes[3] carried out by the same method, a smaller amount of cyclotrimer than in this experiment was supposed to be present between the plateaus of dimer and linear trimer, but it could not be isolated.

Preparation of the Ethylisopropoxypolysiloxanes of the Series (C): (Exp. 4 and 5).—In experiments 4 and 5, ethyldiisopropoxychlorosilane (II) and tetraisopropoxysilane (IV) or hexaisopropoxydisiloxane (V) were refluxed until the mixture became chlorine free.

Analysis of Silicon.—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

Summary

(1) Ethylisopropoxychlorosilanes have been prepared and characterized.

(2) By the thermal reaction of partially isopropanolysis product of ethyltrichlorosilane, linear ethylisopropoxypolysiloxanes containing from 1 to 3 silicon atoms and cyclotrisiloxane have been prepared and characterized.

(3) Ethyldiisopropoxychlorosilane and isopropoxypolysiloxanes were refluxed and the two compounds of the series of linear ethylisopropoxypolysiloxanes in which one terminal group is the ethyl one have been synthesized and characterized.

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Thermionic Emission from Catalyst for Ammonia Synthesis. I. Electron Microscopic Images of the Catalysts

By Hiroshi UCHIDA and Naoyuki TODO

(Received June 12, 1954)

Introduction

Potash is an important promoter used in iron catalysts for ammonia synthesis and Fischer-Tropsch synthesis. On heating the catalyst, potash or potassium becomes liable to emit electrons or potassium ions from the surface. In this connection, C.H. Kunsman[1] measured thermionic emission from iron catalysts for ammonia synthesis already in 1926 and recently Y. Osumi[2] observed the electronic emission image of the catalyst in the oxidic as well as the reduced state and attained to notably interesting results in comparison with the optical. It can be readily understood that the measurements of the thermoelectronic emission provide detailed knowledge on the state of potash in the catalyst. The authors studied accordingly the thermoionic emission by means of the electronic image observation as well as the quantitative thermionic measurement on the catalysts whose catalytic activity for ammonia synthesis, microscopic structure and surface structure, such as area and average pore size, had already been investigated. Results

1) C. H. Kunsman, *J. Phys. Chem.*, **30**, 535 (1926).
2) Y. Osumi, This Bulletin, **26**, 515 (1953).

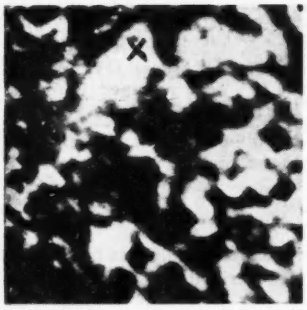

Fig. 1a. Cat. No. 1
Electronic image (830°C)
(Oxide) ×40

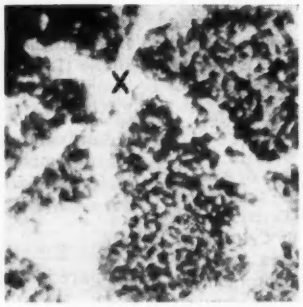

Fig. 1b. Cat. No. 1
Electronic image (450°C)
(Reduced for 5 min.)

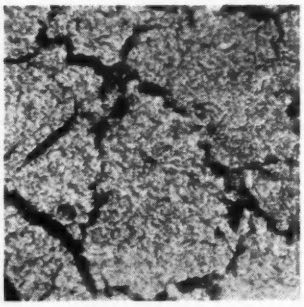

Fig. 1c. Cat. No. 1
Optical image
(After electr. emis.)

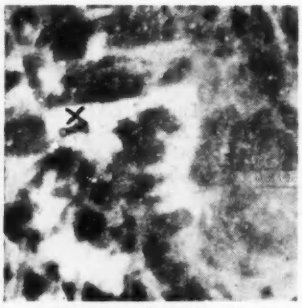

Fig. 2a. Cat. No. 2
Electronic image (870°C)
(Oxide)

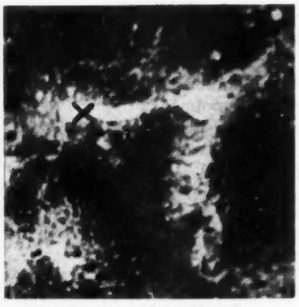

Fig. 2b. Cat. No. 2
Electronic image (680°C)
(Reduced for 20 min.)

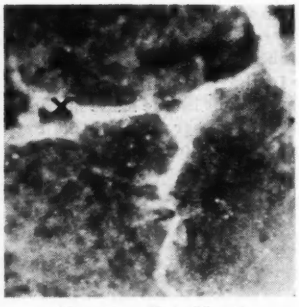

Fig. 2c. Cat. No. 2
Electronic image (760°C)
(After 30 min. observ. of
Fig. 2b)

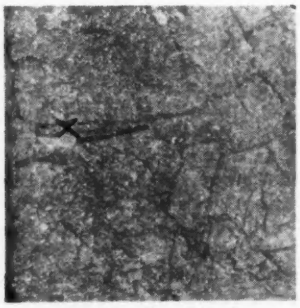

Fig. 2d. Cat. No. 2
Optical image
(After electr. emis.)

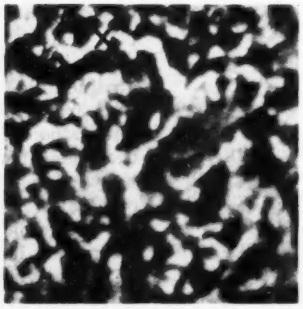

Fig. 3a. Cat. No. 3
Electronic image (800°C)
(Oxide)

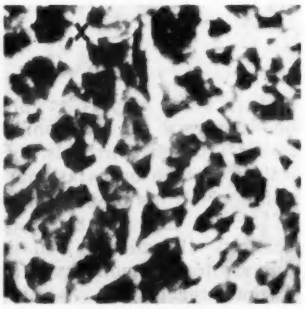

Fig. 3b. Cat. No. 3
Electronic image (780°C)
(Reduced for 5 min.)

obtained on the electronic image observation have lead to a qualitative understanding of potash in the synthetic ammonia catalyst. The results on this thesis will be described in this paper, while the quantitative measurement will be described in the next.

Experimental

Procedures.—The surface electron microscope was of similar type to that used by N. Sasaki[3] and Y. Osumi[2]. Specimens for the electron microscope examination were prepared by polishing with emery paper, finishing with grade 0.5 and finally on cloth to get rid of emery dust from voids. They were of 4 mm. in diam. and 1–1.2 mm. in thickness. The temperature could be raised by heating tungsten filament inserted into the specimen holder and was measured by means of a thermocouple spot-welded as close as possible to the specimen. After the electronic images had been observed on oxidic state, the oxide was reduced at 450°C by passing hydrogen through the microscope at normal pressure. The reduction was stopped at intervals to observe successive alternation of the electronic image. Immediately after the electronic observations, the specimens were removed from the electron microscope to an optical microscope under which they were observed by oblique illumination so that a fair estimate of cracks and hollows on the section was facilitated. The specimens were fused synthetic ammonia catalysts prepared according to a procedure by G. Shima and one of the authors[4] and of the following respective different compositions of the promoters, No. 1: 1% K_2O, No. 2: 5% Al_2O_3, 1% K_2O, No. 3: 4% Al_2O_3, 1% CaO, 1% K_2O, No. 4: 3% Al_2O_3, 2% SiO_2, 1% K_2O, No. 5: 3% Al_2O_3, 2% SiO_2, 1% CaO, 1% MgO, 2.5% K_2O. Their actual potash content was determined by the use of hexyl calcium and found somewhat less than what was expected from the composition of raw material, as shown below respectively, No. 1: 0.86%, No. 2: 0.81%, No. 3: 0.89%, No. 4: 0.71%, No. 5: 1.91%.

Experimental Results

The electronic images are shown from Figs. 1 through 5, in each of which the magnification factor is 40 with an exception of Fig. 4 (×60), together with respective optical micrographs after the electronic observations.*

Catalyst No. 1.—At an earlier stage of 3 minutes, observations showed a bright net work of the emission which gradually decreased in brightness to Fig. 1a which remained almost the same for additional 10 minutes. On reducing the oxide for five minutes, a bright and quite different net work of the emission appeared at such a low temperature as that of 450°C (Fig. 1b). Besides this image, there was not found any homogeneous emission which used to appear on the catalysts containing alumina. On raising the temperature to 750°C, the emission rapidly disappeared. The subsequent optical image is shown in Fig. 1c. In comparison with Figs.1a, b and c, the cracks in the optical image coincide accurately with the net works of Fig.1b, whereas they do not with Fig. 1a.

Catalyst No. 2.—Bright emission patterns were observed together with weaker emission over the whole surface of the oxide (Fig. 2a). On reduction, twenty minutes were required until an abrupt and a very marked change of the image took place as is shown in Fig. 2b. A part of the emissions from the oxide disappeared and new assemblages of fine bright specks appeared. On continuing the reduction for thirty minutes, the specks disappeared and the emission became rather homogeneous over the whole surface across which a few emission bands still shone.** Cracks and a few particular grains surrounded with cracks on the optical image (Fig. 2d) corresponded exactly to the places where the brighter emissions took place on Fig. 2b.

Catalyst No. 3.—As is shown in Fig. 3a, emission images with marked contrast developing appeared on the oxide. A few minutes after the beginning of reduction, the image changed abruptly to a new net work almost independent of the image in the oxide (Fig. 3b). On the continued observations, the emissions decreased in number and brightness till to Fig. 3c which could be closely related to the optical image (Fig. 3d).***

Catalyst No. 4.—The emission was so weak that the image could hardly be observed at the temperatures below 880°C (Fig. 4a). As it had been reported[5], the catalyst, added with silica, contained glassy inclusions on the polished section of the oxide (Fig. 4b). When the emission images were compared with the optical on the oxide, it could readily be detected that the bright emissions occurred from the glassy inclusions. The major part of the emission images remained after the reduction.

Catalyst No. 5.—The emissions became suf-

3) N. Sasaki, R. Ueda. T. Kuroda and H. Okamoto, *J. Soc. Metal, Japan*, **16**, 165 (1950).

4) G. Shima and H. Uchida, *Rep. Chem. Ind. Res. Instit. Tokyo*, **45**, 369 (1950).

* A paper provided with more of photographs will be published in the *Rep. Chem. Ind. Res. Instit., Tokyo.*

** On the electronic images from the oxide, there were observed black specks which began to shine after the oxide was reduced for 20 minutes; specks of this sort were observed only on catalyst No. 2 and the nature has not been accounted for in this paper.

*** When magnesia was used instead of lime, there were not found any emissios on the oxide except for those from the places corresponding to the cracks.

ficient to be observed at 780°C. Among the emission images, some took crystalline appearances (Fig. 5a), corresponding to the crystalline inclusions* which used to appear on the polished sections with increasing amounts of potash, as reported previously[5]. On reduction, the images of crystalline outline remained, whereas those of narrower bands and specks disappeared, and a rather homogeneous emission over the whole surface associated with a number of new narrow bands appeared (Fig. 5b). The emission image obtained after the reduction relates to the optical (Fig. 5c) similar to the findings with catalyst No. 2.

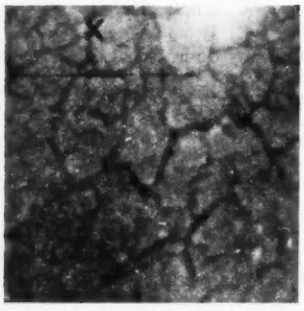

Fig. 3c. Cat. No. 3
Electronic image (850°C)
(After 5 min. observ. of Fig. 3b)

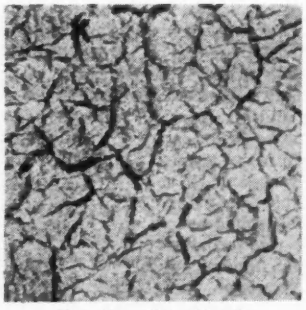

Fig. 3d. Cat. No. 3
Optical image
(After electr. emis.)

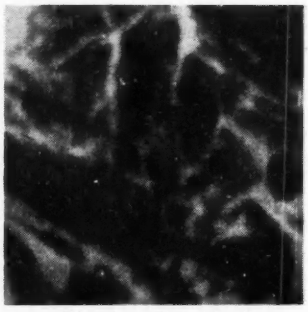

Fig. 4a. Cat. No. 4
Electronic image (900°C)
(Oxide) (×60)

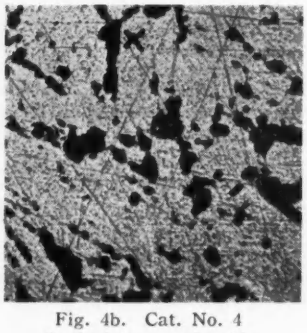

Fig. 4b. Cat. No. 4
Optical image of oxide
by vertical illuminat.
(×60)

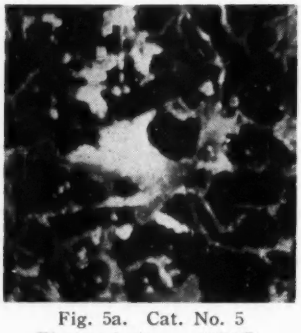

Fig. 5a. Cat. No. 5
Electronic image (850°C)
(Oxide) ×40

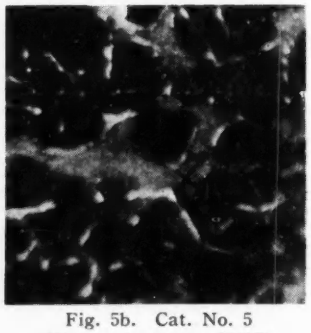

Fig. 5b. Cat. No. 5
Electronic image (780°C)
(Reduced for 5 min.)

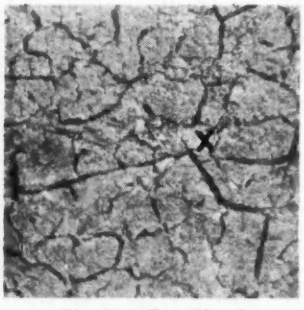

Fig. 5c. Cat. No. 5
Optical image
(After electr. emis.)

Grain Boundary.—On polishing on emery paper and then with red iron oxide on a rotating pad, well marked grain boundaries by ordinary vertical illumination were developed by etching with hydrochloric acid as shown in Fig. 7 at a magnification of X 100. Broader grain boundaries enclose large grains (parent grain) which are divided into a number of fine fragments by unifrom orientation of etch marks on the grains. The catalyst consists of a mosaic like structure of such fine

* On catalyst No. 5, the inclusions could be observed only on the section thoroughly polished with red iron oxide on a rotating pad, in use of which the electronic emission observations were difficult to investigate.

5) H. Uchida, N. Todo and K. Ogawa, *Rep. Chem Ind. Res. Instit., Tokyo*, **46**, 11 (1951).

grains***. Though the specimens polished to such an extent that they were used for the electron emission revealed also patterns shown in Fig. 6, they could be by no means related to the grain boundaries in Fig. 7. It has thus proved that a prediction of grain boundaries from optical patterns on the specimen prepared for the electronic emission is a matter of considerable difficulty. On the other hand, when the section of Fig. 7 was reduced, every crack developed along the etch marks, i. e. the grain boundaries Fig. 9. This could be also confirmed on the other catalysts.

Discussion

It may be estimated with certainty that electrons may easily emit from the place rich in potash or potassium. If additives were always liable to accumulate in the grain boundaries of the oxide, the electronic emission would take place along the boundaries. In this respect, reference is made to a recent article by Y. Osumi[2] who has thought electrons emit mainly from the parts which existed at the grain boundaries as a result of his electronic and optical images comparison. He called this particular part B, distinguishing itself from another part A more abundant in the catalyst. However, in our observations, marked changes of the emission images took place frequently in course of reduction and the places on which the emission was observed in the oxidic state frequently did not correspond to those in the reduced state. Furthermore, the net works of the emission from the reduced, which are quite different from those from oxides, always coincide exactly with the grain boundaries. It, therefore, can not be said reasonably that the emission images from the oxides correspond always to the grain boundaries. Alternation of the emission images in course of the reduction occurred in different manners as described before. Among them, those which were observed on both the oxidic and the reduced were either of relatively wide bands (catalyst No. 2 and 3), or of crystalline outline (catalyst No. 5). Cracks were observed around them on the optical image. They may correspond to interfacial crystallites or grains rather than grain boundaries and the promotors such as potash may segregate in such particular grains. Y. Osumi has already observed that bright emission occurres along the cracks produced by reduction and the fact has been interpreted by himself as being due to migration of active substance such as potash or potassium from beneath to the surface by way of the cracks. The beautiful net work of the emission which coincides with the cracks may therefore give a measure for estimation of the cracks; however, it is not directly related to distribution of potash or potassium in the catalyst. Information concerning the distribution in the oxide may be afforded by another kind of the emission images, which is observed in the oxidic, but is scarcely ever observed at the same places in the reduced. The particular regions where the above kind of the image appears will be searched on the polished and etched section of catalyst No. 3 under an optical microscope. By ordinary vertical illumination (Fig. 7), there are found in the parent grain several shining areas which appear as voids when observed by oblique illumination (Fig. 8). The shining is due to the surface of the grains underlying these having dissolved out with hydrochloric acid. The voids could also be observed more or less marked on the other catalysts; for example, on catalyst No. 2, they were shallow and the areas shining by vertical

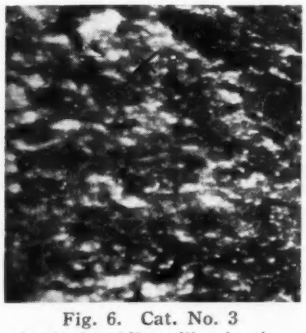

Fig. 6. Cat. No. 3
Oxide by oblique illumination
×100

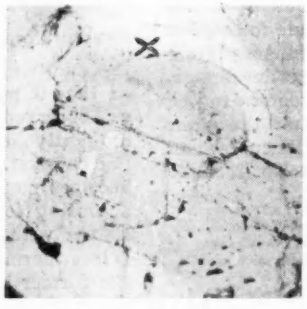

Fig. 7. Cat. No. 3
Oxide by vertical illumination (Thoroughly polished and etched surface)

Fig. 8. Cat. No. 3
Fig. 7 by Oblique illumination

illumination were hardly observed. The parent grain may be thus estimated to be divided into those sub-grains which are readily etched with hydrochloric acid and those which are etched with difficulty more or less markedly according to the kind of the catalysts. The voids thus observed on catalyst No. 3 are mostly like the emission images from the oxide in shape and dimension. Since the subgrains readily etched are expected to be rich in potash and to be liable to emit electrons, the bright emission images on the oxide may well be related to the voids, that is to say, to the sub-grains which existed at the voids before they were dissolved out by hydrochloric acid.

Fig. 9. Cat. No. 3
Reduced surface of Fig. 8

On the catalysts No. 2, 3 and 4, the catalytic activities for ammonia synthesis were measured at a pressure of 100 kg./cm², and the surface areas*, the surface concentrations of potash (+lime)**, the average pore radii*** were also measured on the specimens after the use for the activity measurements[6]. The results are shown again in Fig. 10 and Table I together with those on catalyst No. 5 respectively. A catalyst promoted with alumina, potash and magnesia instead of lime has almost the same activity as catalyst No. 2 (Fig. 10). An attempt will be made to account for promoting action of the additives from the view point of the electron emission image. On adding alumina, potash seems to be stabilized in view of the fact that the emissions were retained over the whole surface on prolonged heating with catalyst No. 2, while

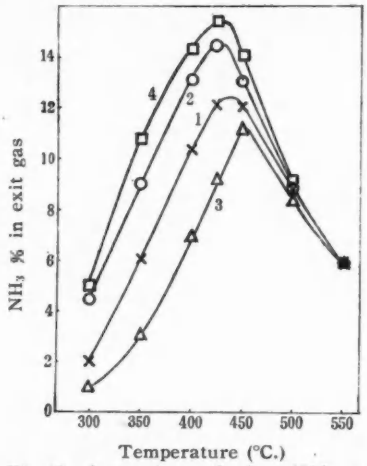

Fig. 10. Ammonia synthesis at 100 kg./cm² and S.V. 5000 in use of 20 cc. Cat.
1; No. 2, 2; No. 3, 3; No. 4, 4; No. 5

they disappeared rapidly with catalyst No. 1. Excellent dispersion of potash is thus observed from the emission image of catalyst No. 2. An addition of lime causes an appreciable increase of the activity as well as the markedly heterogeneous emission which is estimated to be due to the particular subgrains as described above. When magnesia was used instead of lime, there have been found neither the increase of the activity nor the heterogenous emission. The promoting actions of lime for the activity are thus probably ascribed partially to its effect for the formation of the well marked sub-grains in the parent grains, besides that of increasing the surface area (ref. Table I). As for

TABLE I

Catalyst	No. 2	No. 3	No. 4	No. 5
Surface Area, m²/g.	6.11	8.48	7.21	6.0
Surface Concentration of Potash	0.61	0.56	0.20	0.74
Average Pore Radius, Å	400	301	322	460

the addition of lime, A. Nielsen[7] has described that it makes the phase less anisotropic as observed by polarized light and consequently increases the thermostability of the catalyst. On the contrary the surface becomes more heterogeneous on the addition according to our observation and this is consistent with our results[8] that catalyst No. 3 is less thermostable than catalyst No. 2, while the former is superior in the activity to the latter.

** By means of observation under electron microscope on replica of the etched surface, the grains seemed to consist of fine crystallites as small as a few microns in diameter.

* Calculated from isotherms of physical adsorption of CO_2 by means of BET method.

** Represented by ratio of value of chemisorbed CO_2 to that of monomolecular adsorption at 78°C.

*** Average pore radius is calculated by $r=2\times v/S$, where v is pore volume (volume by mercury displacement-volume by water displacement) and S, surface area.

6) H. Uchida and N. Todo, *J. Chem. Soc. Japan* (Industr. Sect.), **56**, 225 (1953).

7) A. Nielsen, "Advances in Catalysis and Related Subjects," Academic Press Inc., New York, **5**, 1 (1953).

8) H. Uchida, *Rep. Chem. Ind. Res. Instit. Tokyo*, **46**, 1 (1951).

On the microscopic examination of catalyst No. 4 containing sillca, glassy grains are present. As potash is liable to segregate in these grains as described, potash is poorer in the major surface free from these grains than it is in catalyst No. 2 and 3, since the total content is almost the same in every three. The part played by the addition of silica may therefore reduce the surface concentration of potash and consequently cause a decrease of the activity. From this view point, a simultaneous addition of potash sufficient to spread in every grain of catalyst with addition of sillica will probably contribute to a recovery of the activity. The estimation is confirmed with the results with catalyst No. 5.

H. Kobayashi et al[9] have found recently that potash can be divided into those soluble in water and those insoluble and that the larger the content of the latter the higher the activity for ammonia synthesis. They have also described a relation between them, according to which a rapid linear increase of the activity is accompanied with the insoluble potash content till to 0.4% potash, beyond which the increase becomes gradually more slow, showing a bend at this content. The value of 0.4% has been considered by them as a limiting content of potash in A part by Y. Osumi. As has been indicated by H. Kobayashi, the activity remains quite low as far as the insoluble content dose not exceed 0.4%. It is therefore necessary to increase the content more and more to obtain any catalyst appropriate for the industrial use. On the basis of our results on the optical as well as the electronic emission images, potash in excess of that possessed by the catalyst distributed homogeneously in the bulk is found locally in the following three kinds of the regions such as, 1 grain boundaries, 2 particular sub-grains in the parent grains, 3 interfacial grain (glassy or crystlline) especially in the particular case where promoters such as silica are used. On reducing the catalysts, they afford a large surface area as shown in Table I respectively. Among the above three, the grain boundaries might contribute to a very small area even if the grains were of the dimension of a few microns. Secondly, the interfacial grains occupy only a small fraction of the total number of the grains and their presence seems not to contribute to an increase of the surface area as well as the activity as it is proved on the latter with catalyst No. 4. In contrast, the particular sub-grains may most contribute to the surface area, as they occupy a wide region of the grains wherein numerous fine pores appear on reduction. It may therefore be probable that the insoluble potash exceeding the limiting value of 0.4% may exist in these sub-grains, so this fact may contribute most to the activity. These sub-grains are liable to appear markedly on addition of lime, and, ndeed the catalyst shows high activity. The authors would finally like to mention that the appearance of the particular sub-grains may be accelerated not only in use of adequate promoters, but may also be favored by maintaining the temperature during the fusion as high as possible so that the segregation of potash in the grain boundaries may be avoided.

9) H. Kobayashi and O. Nishijima, *J. Chem. Soc. Japan* (Industr. Sect.), **57**, 189 (1954).

Summary

The electronic images have been observed on 5 types of the catalysts for ammonia synthesis, which are different in promoter-composition. On heating the oxides from 750 to 900°C, the images of different kinds which were characterized by their respective promoters compositions appeared after a few minutes. On reduction, some of the images remained, while the others disappeared, and during the periods of five to thirty minutes of the reduction, the images turned to the respective characteristic ones again, sometimes being quite different from those of the oxides. On the additional observations, a part of the images weakened or disappeared and rather the homogeneous images over the whole sections became to be observed by raising thetemperature.

Comparing the image with the optical, the net work of the emission after the reduction corresponds to cracks on the section. When the microscopic structure of the section thoroughly polished and etched with hydrochloric acid is adopted for comparison with the above optical image, grain boundaries in the oxide always correspond to the cracks. Therefore, the electronic images on the oxide are not always related to the grain boundaries.

Qualitative explanations on respective promoting effect of alumina, lime and silica are yielded from view point of the electronic image.

It has been proved from the observations of the electronic as well as the optical images that there are the following 3 types of regions which are rich in potash, i.e. the grain boundaries, particular interfacial grains and some of the sub-grains into which the

parent grains are divided. When references are made to the results of the activity for ammonia synthesis, surface area and etc., together with that by H. Kobayashi who has described that the activity is greatly enhanced by the larger amount of potash insoluble in water, the estimation shows that probably potash existing in the sub-grains above may most contribute to the activity for ammonia synthesis.

The authors wish to express their sincere thanks to Professor Nobuji Sasaki and Mr. Ryuzo Ueda of Kyoto University for their valuable advice concerning the electron microscope.

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The Effect of Solvent on Infrared Absorption Bands of Halogenated Hydrocarbon Molecules

By Tsuneo YOSHINO

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The intensities of infrared absorption bands have hitherto been measured with two main objects, namely for qualitative and quantitative analyses and for elucidating structural problems, and most of the measurements have been made in solution because the measurements in gaseous state are often difficult. Nevertheless the effects of solvent on infrared absorption bands have scarcely been studied except for the particular case where the hydrogen bond is concerned, and the intensity of the band, especially the area intensity of the band, has often been assumed to be independent of the solvent used. Recently Whiffen[1] has measured an infrared absorption band of chloroform near 760 cm^{-1} and has concluded that the area of the band is approximately independent of solvents although the peak height and the width at half height change considerably with them.

The present work was undertaken to see the effects of solvents on some degenerate and non-degenerate infrared absorption bands of polar and non-polar halogenated hydrocarbon molecules. In particular it seems to be of interest to know whether or not the band area is kept constant for the variety of solvents.

Experimental

Absorption measurements were made for the bands of carbon tetrabromide[2], *cis*-1,4-dibromocyclohexane and *trans*-1,4-dichlorocyclohexane. Following Bartal's method[3] carbon tetrabromide was prepared from acetone and bromine. (m.p. 93°C). The absorption band measured for this compound is the triply degenerate one, the peak frequency of which is about 670 cm^{-1}.

cis-1,4-Dibromocyclohexane[4] was synthesized from chinit and hydrobromic acid by the method used by Rothstein[5] and was separated from *trans*-1,4-dibromocyclohexane by fractional crystalizations using petroleum ether and methanol as solvents, repeatedly one after another. (m.p. 49°C)[6]. The purity was certified by the infrared inspection. The solvent effect was measured for the nine strong bands in the region from 7 to 23μ.

trans-1,4-Dichlorocyclohexane was made from chinit and hydrochloric acid by Rothstein's method[5]. (m.p. 102°C). This compound has two isomeric forms, the abundance ratio of which changes with solvents[7,8]. The solvent effects were, therefore, observed only for the changes of band widths and peak frequencies. The peak frequencies were measured for the bands in the region from 7 to 23μ, but the half intensity widths were measured only for the bands near 475, 565, 760 and 785 cm^{-1}, because the bands of two isomers above 800 cm^{-1} appear in close pairs and the band widths, therefore, cannot be measured accurately.

The spectral data were obtained with Perkin-Elmer Model 112 spectrometer with KBr prism for the region from 14 to 23μ and with NaCl prism for the region from 7 to 14μ. The thicknesses of cells used were 0.102 and 0.103 mm.

1) D.H. Whiffen, *Trans. Faraday Soc.*, **49**, 878 (1953).

2) Since one of the two infrared active bands of carbon tetrachloride lies in the region where KBr is not transparent and the other appears near 780 cm^{-1} as doublet (Fermi resonance), this compound is not suitable to use for the present purpose.

3) A. Bartal, *Chem. Zt.*, **29**, 377 (1905).

4) Detailed report on this compound by Kozima and Yoshino will be soon published in other place.

5) M.B. Rothstein, *Ann. chim.*, **14**, 461 (1930).

6) m.p. in literatures is 43°C or lower. See, for example, 5) or E. L. Bennett and C. Niemann, *J. Am. Chem. Soc.*, **74**, 5076 (1952).

7) K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).

8) T. Yoshino, *J. Chem. Soc. Japan*, **75**, 592 (1954).

which were measured with the interference method. The slit width employed was such that the spectral slit width was nearly equal to, or narrower than half of the half intensity width and kept constant for the variety of solvents. The spectral slit width S was calculated[9] by the following formula, which was obtained by the simple modification of the formula[10] for single pass spectrometer,

$$S=\tilde{\nu}^2\frac{[1-n^2\sin^2(\alpha/2)]^{1/2}}{8\sin(\alpha/2)(dn/d\lambda)}\frac{s}{f}+\frac{\tilde{\nu}}{4l(dn/d\lambda)}$$

where $\tilde{\nu}$ is frequency in cm^{-1}, n is index of refraction at frequency $\tilde{\nu}$, α is prism apex angle, $dn/d\lambda$ is dispersion of prism material, and s, f and l are the slit width, the focal length and the length of prism base in cm. unit respectively.

The absorption curves of solvent and solution were recorded using the same cell, and constancy of recording condition was checked before and after each measurement using the reference cell filled with solvent. Errors due to stray light and non linearity of the amplifier were negligible.

Results and Discussions

The abbreviations used in this paper are as follows:

$\tilde{\nu}_{max}$ = frequency at the peak in cm^{-1}.

ε_{max} = apparent peak intensity in $10^5\,cm^{-1}$ $mol.^{-1}$. The base of logarithm is 10.

ε_{max} (corr.) = peak intensity in $10^5\,cm^{-1}$ $mol.^{-1}$, with Ramsay's slit-width correction[11], assuming Lorentzian curve:

$$a=B/[b^2+(\tilde{\nu}-\tilde{\nu}_0)^2].$$

b' = frequency interval in cm^{-1} between the band center and the half height position on long wave length side.

b'' = the same one on the short wave length side.

$2b=b'+b''$.

$2b$ (corr.) = $2b$ value with slit-width correction.

$\int\varepsilon d\nu$ = band area in $10^{10}\,cm^2$ $sec.^{-1}$ $mol.^{-1}$.

$\log I_0/I$ = absorbance at the peak used to correct ε_{max} and b.

range = integration range in cm^{-1}. Except for the carbon tetrabromide band, the integration range is taken so that the absorption peak lies in its center.

First of all, let us consider the band of carbon tetrabromide. The results are shown in Table I for the various solvents used. The frequencies of the absorption peak in dioxane and in ethyl acetate are higher than those in *n*-heptane and in carbon tetrachloride. These results do not agree with Whiffen's results for chloroform band, which show that the peak frequency becomes highest in *n*-heptane and lowest in dioxane and in general is higher in non-polar solvents and lower in polar solvents.

The apparent half intensity width of the carbon tetrabromide band changes very much with solvents and is smaller in *n*-heptane and in carbon tetrachloride and larger in dioxane and ethyl acetate in accordance with the results of the chloroform band. We see, therefore, that in the carbon tetrabromide band the wider absorption is not accompanied with lower value of peak frequency as was mentioned in reference to the chloroform band.

The large half intensity width is accompanied by the low absorption peak, as is shown in Table I, so that the band areas in various solutions are brought near a definite value, but the differences of the areas are greater than the experimental error. The band area is larger in the solvent which lowers the peak frequency.

Table I

Solvent	$\tilde{\nu}_{max}$	ε_{max}	b'	b''	$\int\varepsilon d\nu$	$\log I_0/I$
dioxane	674.8	2.87	14.1	9.3	22.4	0.39
ethyl acetate	672.9	3.05	11.4	13.1	24.1	0.39
n-heptane	672.5	9.15	4.4	3.7	23.8	0.47
carbon tetrachloride	671.8	7.39	5.5	4.8	27.0	0.38

$2S=8.3$

The values of area intensities in Table I were integrated over the frequency ranges from $\tilde{\nu}_{max}-3b'$ to $\tilde{\nu}_{max}+3b''$ cm^{-1}. The band shapes are not symmetric, namely b' is not equal to b''. The solvent changes not only b' and b'' but also the ratio of them. The absorption curve, especially on the high frequency side of the peak, does not fit the Lorentzian curve even if the slit-width correction is made. The absorbance at $\tilde{\nu}_{max}-3b'$ and at $\tilde{\nu}_{max}+3b''$ are about 1/20 and 1/40 of that at the peak respectively and are smaller than those obtained from the Lorentzian

9) The values of n and $dn/d\lambda$ were takec from: C. Schäffer and F. Matossi, "Das Ultraroc Spektrum", Julius Springer, Berlin (for NaCl) and R. E. Stephens, E. K. Plyler, W. S. Rodny and R. J. Spindler, *J. Opt. Soc. Am.*, **43**, 110 (1953) (for KBr).

10) For example, van Z. Williams, *Rev. Sci. Inst.*, **19**, 135 (1948).

11) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

curve (1/10) by use of the peak height and the b' or b'' value with slit-width corrections. Owing to rather rapid decrease of absorption on the wings outwards from the center, the sum of the areas outside of the integration range may by estimated to be about one tenth of the band area and the ratio may not vary with solvents. Therefore the values of band areas in Table I integrated over the finite regions may be used for the comparison of band areas in various solutions in place of the values of infinite integration ranges.

The results of the measurements of the bands of *cis*-1,4-dibromocyclohexane near 505, 640 and 740 cm^{-1} are given in Tables II and III. The shapes of these bands are approximately the Lorentzian form. The Lorentzian curve suitable for the region near the band center does not accurately fit the wings and has a little larger value of absorbance than that observed. The peak frequencies of these bands take lower values in benzene, dioxane and polar solvents and the lower peak frequencies are accompanied with the wider half intensity widths. These effects are in accordance with those observed for chloroform band but the changes of the band widths with solvents are not so large as those in the degenerate bands of carbon tetrabromide and chloroform.

The wings of the absorption band spread over very wide ranges and the area in the wings is not negligible in spite of the small absorbances in the wingths. But as it is hard to obtain the area in the wings with accuracy, the values in Tables II and III were integrated over the definite spectral intervals of about four times of the half intensity widths. The band areas shown in the Table increase with solvents which lower the peak frequency and broaden the band. The area outside of the integration range and its ratio to the integrated area of the broadened band are larger than those of the narrowed band.

TABLE II

Solvnet	$\tilde{\nu}_{max}$ or $\Delta\tilde{\nu}_{max}$	ε_{max}	ε_{max} (corr.)	$2b$	$2b$ (corr.)	$\int \varepsilon d\nu$	$\log I_0/I$
n-heptane	506	0.57	0.63	6.6	5.8	1.43	0.30
cyclohexane	−0.0	0.60	0.67	6.1	5.3	1.39	0.30
carbon tetrachloride	−0.9	0.62	0.67	6.6	5.9	1.48	0.36
benzene	−3.2	0.62	0.67	7.1	6.4	1.61	0.36
chloroform	−3.2	0.56	0.59	8.2	7.6	1.58	0.32
elthyl acetate	−3.6	0.52	0.55	8.1	7.5	1.52	0.34
dioxane	−3.6	0.57	0.59	8.2	7.6	1.71	0.32
n-heptane	645	1.07	1.30	7.3	5.8	2.99	0.28
cyclohexane	−0.0	1.05	1.27	7.3	5.8	2.90	0.30
carbon tetrachloride	−1.1	1.09	1.30	7.5	6.0	3.10	0.31
chloroform	−3.5	1.11	1.25	8.6	7.3	3.18	0.31
cyclohexane	739	0.93	1.19	4.5	3.3	1.61	0.29
benzene	−2.3	0.95*	1.2 *	4.6*	3.4*	1.7 *	0.31*
dioxane	−2.7	1.01	1.24	4.8	3.7	1.88	0.36

$2S$=4.7, 7.0, 4.7, range=23.5, 32.7, 17.7, for the bands near 505, 640, 740 cm^{-1} respectively.
* These values are inaccurate because of the absorption of the solvent.

TABLE III

Solvent	$2S$	ε_{max}	ε_{max} (corr.)	$2b$	$2b$ (corr.)	$\int \varepsilon d\nu$	$\log I_0/I$
dioxane	3.4	0.57	0.59	8.0	7.7	1.71	0.32
	4.7	0.57	0.59	8.2	7.6	1.71	0.32
	6.7	0.56	0.62	8.7	7.6	1.72	0.31
	8.7	0.52	0.61	9.5	7.6	1.70	0.28
n-heptane	3.4	0.59	0.61	6.4	6.0	1.43	0.31
	4.7	0.57	0.63	6.6	5.8	1.43	0.30
	6.7	0.51	0.61	7.2	5.7	1.39	0.27
	8.7	0.47	0.63	7.7	5.4	1.31	0.25

$2S$=23.5

For the absorption curve of dioxane solution, Lorentzian form is a good approximation. Assuming the Lorentzian curve with B_i/b^2=0.59 and $2b$=7.6, the area intensity with infinite integration range is 2.12 which is 24% larger than the value in the Table.

Then the increment of the band areas above mentioned is not diminished even if integrated over the infinite range. As the areas outsied of the integration ranges in various solutions are different from each other only by a small percent of the integrated area, the increment of band area integrated over infinite range is approximately the same as that shown in Table II and might not exceed 30% for the 505 cm^{-1} band in which the increment is largest.

The transmission measured is the average of the transmissions for the interval of the slit width. Therefore the band area measured, particularly when the integration range is limited, might be smaller than that with infinitely small slit width and this diminution might depend upon the ratio of the band width to the spectral slit width. The area of the band near 505 cm^{-1} was measured with various slit widths for the *n*-heptane (which narrows the band width) and dioxane (which broadens the band width) solutions, but the band areas were found to be independent of slit width as shown in Table III so far as the half intensity width is smaller than twice the spectral slit width. The change in the ratio of the band width to the slit width, therefore, does not make any contribution to the change of the band area with solvents.

The decrease of the band areas in *n*-heptane and cyclohexane is not due to the change of molecules from one form to the other. The reason for this is as follows. As all the bands below 800 cm^{-1} decrease their intensities in the same manner in these solvents, they must belong to one form which is much more populated than the other. Owing to the change of molecules which causes the decrease of the band areas observed, the increase of the band areas of less populated form, if it exists, should be remarkable so far as any of the bands is not covered by the absorption of the more populated form or has appreciable absorbance. But none of the bands which show such a remarkable increase of band area in *n*-heptane or in cyclohexane solution was found in the region from 7 to 23μ. Thus we can see that the change of area intensity without change of molecules takes place for the bands of this compound. Such a change of band area has also been observed for the C=O stretching bands of ketones[12] in chloroform and carbon tetrachloride in accordance with the present results.

In carbon tetrachloride solution the frequency, width and area of the absorption band take intermediate values of those in polar and non-polar solvents.

The shapes of the bands above 800 cm^{-1} are also nearly Loretzian form and the band widths change with solvents as the bands below 800 cm^{-1}. But some of the solvent effects on the higher frequency bands are different from that described before. The peak frequencies of these bands, as shown in Table IV, do not change with solvents and the change of band areas is not

Table IV

$\bar{\nu}_{max}$	$2S$	Range	Solvent	ε_{max}	$2b$	$\int \varepsilon d\nu$
872	3.7	26.3	carbon tetrachloride	1.16	5.3	2.5
			benzene	1.06	5.5	2.4
			chloroform	1.23	5.4	2.7
991	4.2	21.3	cyclohexane	1.68	4.0	2.8
			carbon tetrachloride	1.74	3.9	2.8
			chloroform	1.80	4.1	3.2
			dioxane	1.55	4.5	2.8
1162	5.1	32.5	cyclohexane	0.78	6.4	2.1
			carbon tetrachloride	0.78	6.5	2.1
1206	5.2	30.3	cyclohexane	1.14	7.9	3.5
			carbon tetrachloride	1.12	8.3	3.5
			benzene	1.07	9.7	3.7
1259	5.4	40.6	carbon tetrachloride	1.65	7.1	4.8
			benzene	1.71	7.7	5.3
1341	6.1	22.1	cyclohexane	0.91*	5.9*	2.2*
			carbon tetrachloride	1.09	5.4	2.4
			benzene	0.99	5.5	2.3
			chloroform	1.11	5.7	2.5

* These values are inaccurate because of the absorption of the solvent.

12) G. M. Barrow, *J. Chem Phys.*, **21**, 2008 (1953).

TABLE V

Solvent	2S	ν_{max} or $\Delta\nu_{max}$	2b	2b (corr.)	log I_0/I
cyclohexane		476	5.2	3.8	0.24
carbon tetrachloride	5.6	−0.8	5.2	3.9	0.41
benzene		−2.0	5.4	4.1	0.35
cyclohexane		566	7.3	6.7	0.48
carbon tetrachloride	4.5	−2.2	7.8	7.3	0.81
benzene		−4.5	8.0	7.5	0.45
cyclohexane		759	3.5	2.9	0.64
benzene	3.3	−3.2	4.1	3.5	0.46
dioxane		−4.2	5.0	4.4	0.43
cyclohexane		786	4.5	3.8	0.40
benzene	3.7	−3.8	5.6	5.1	0.47
dioxane		−4.9	6.0	5.5	0.55

the same for all these six bands nor analogous to that mentioned to the lower frequency bands.

For the bands of *trans*-1,4-dichlorocyclohexane, the solvent effect on the peak frequencies and the widths shown in Table V is the same as that described for the bands of *cis*-1,4-dibromocyclohexane. The peak frequencies of the bands above 800 cm^{-1} which are not given in the Table do not change appreciably with such solvents as cyclohexane, carbon tetrachloride, chloroform and benzene.

So far as the molecules discussed are concerned, the frequency lowering with solvents takes place only for the bands which are related intimately to the stretching and deformation of carbon-halogen bonds. These changes may be due to the perturbation of the solute molecules caused by the action of solvent on the carbon-halogen bonds[13].

We have seen above that the integrated intensity of an absorption band of halogenated hydrocarbon molecules is not kept constant for the variety of solvents and this intensity change is remarkable in low frequency bands. Chako's theory[14] fails to explain this increase of band area, so far as the index of refraction of pure solvent in visible light is used. In this respect it is of interest that the solvent which lowers the peak frequency, broadens the band width and increases the band area is the one which stabilizes the polar form of rotational isomers[15].

In the degenerate bands mentioned above, large changes of band widths and peak heights took place. This remarkable feature might be due to the splitting of degeneracy. The frequency change in the carbon tetrabromide band is different from those in the bands of chloroform and cyclohexane derivatives. This peculiarity of carbon tetrabromide seems to be due to the spherically symmetric form of the molecule and seems to coincide with the action of carbon tetrachloride as non-polar solvents like *n*-heptane and cyclohexane as was seen in the present results.

Acknowledgment

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13) Detailed report on the studies of the solvent-solute interaction using mixed solvents will be published in near future.

14) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

15) The elongated form of *trans*-1,4-dichlorocyclohexane corresponds to the polar form in regard to the solvent effect on the abundance ratio. The correspondence was elucidated in 8).

The Spatial Configurations and the Ultraviolet Absorption Spectra of Biphenyl and Some Related Compounds

By Hiroshi SUZUKI

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It is well-known that atrop-isomerism occurs when two or more of the ortho hydrogen atoms in biphenyl are replaced by larger atoms or groups. This phenomenon is explained as due to steric hindrance which prevents rotation about the central 1-1′ bond in the biphenyl derivatives. These molecules therefore must have a non-coplanar configuration.

Regarding the spatial configuration of biphenyl itself, on the other hand, there appear to be several conflicting evidences. Thus, the results of X-ray crystal analyses of biphenyl showed the molecule to have a completely planar configuration,[1] while electron diffraction investigations suggested a non-coplanar configuration in which the two benzene rings are perpendicular[2] or at an angle of about 45°[3] to each other. When it is assumed that the molecule of biphenyl is coplanar, the distance between the two nearest ortho hydrogen atoms attached to different benzene rings is about 1.8Å, which is considerably shorter than the usual van der Waals distance 2.0Å; therefore, there should be considerable steric interference between them.

The ultraviolet absorption spectrum of biphenyl is quite different from that of benzene and has an intense characteristic band. This is supposed to be due to the conjugation between the two benzene rings, indicating consequently that the molecule of biphenyl is coplanar or nearly coplanar, since it is generally assumed that such conjugation requires the coplanarity of the two benzene rings. On the other hand, the spectra of the derivatives of biphenyl in which the four ortho positions are substituted, e.g., bimesityl, fail to exhibit the characteristic biphenyl band, and are essentially those of the two corresponding benzene compounds.[4] This is explained by the theory that in these compounds the two benzene rings cannot be coplanar owing to steric interference of the ortho substituents[5] and consequently the conjugation between the benzene rings is destroyed. The occurrence of the conjugation between the two benzene rings in biphenyl is also proved by the fact that the extra-resonance energy has been found to be about 8 kcal./mol.[6] or about 5 kcal./mol.[7] for biphenyl, and further suggested by the fact that in *p*-nitro-*p*′-aminobiphenyl the *p*-nitro group exercises a marked effect upon the basicity of the *p*′-amino group and this effect is diminished by ortho substitution by two methyl groups[8], and also by the fact that the dissociation constants of substituted *p*-biphenylcarboxylic acids are influenced by the substituents, the effect being transmitted through the biphenyl system.[9] Furthermore, on the basis of the assumption of the coplanar configuration, London[10] has computed the energy levels of the biphenyl molecule by the method of antisymmetrized products of molecular orbitals with considerably good agreement between the theoretical electronic transitions and the observed ultraviolet absorption spectrum. These seem to be favourable for the coplanar configuration.

It should, however, be here pointed out that the conjugation requires not necessarily the perfect coplanarity. The conjugation operates by the overlapping of the π-orbitals of the 1, 1′ carbon atoms, so it should operate in full at coplanarity. However, partial loss of coplanarity is not necessarily associated with complete loss of conjugation. That is, the

1) (a) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932); *Chem. Abst.*, **26**, 4517. (b) Idem., *Proc. Natl. Inst. Sci. India*, **15**, 11 (1949); *Chem. Abst.*, **43**, 4655.

2) J. L. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 1974 (1944).

3) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949).

4) (a) L. W. Pickett, G. F. Walter and H. France, *J. Am. Chem. Soc.*, **58**, 2296 (1936); (b) M. T. O'Shaughnessy and W. H. Rodebush, ibid., **62**, 2906 (1940).

5) Concerning the effects of ortho substituents on the spectra of biphenyls, see also: (a) M. Pestemer and E. Mayer-Pitch, *Monatsh.*, **70**, 104 (1937); (b) M. Calvin, *J. Org. Chem.*, **4**, 256 (1939); (c) B. Williamson and W. H. Rodebush, *J. Am. Chem. Soc.*, **63**, 3018 (1941); (d) D. W, Sherwood and M. Calvin, ibid., **64**, 1350 (1942); (e) W. H. Rodebush and I. Feldman, ibid., **68**, 896 (1946); (f) R. A. Friedel, M. Orchin, and L. Reggel, ibid., **70**, 199 (1948).

6) (a) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933); L. Pauling, "The Nature of the Chemical Bond", (1939), p. 129; (b) M. Szwarc, *Nature*, **161**, 890 (1948).

7) F. Wm. Cagle and H. Eyring, *J. Am. Chem. Soc.*, **73**, 5628 (1951).

8) D. W. Sherwood and M. Calvin, *J. Am. Chem. Soc.*, **64**, 1350 (1942).

9) E. Berliner and E. A. Blommers, *J. Am. Chem, Soc.*, **73**, 2479 (1951).

10) A. London, *J. Chem. Phys.*, **13**, 396 (1945).

perfect coplanarity is not prerequisite to the occurrence of conjugation and consequently to the appearance of the spectrum characteristic of such a conjugated system.

On the basis of such considerations, the apparently conflicting evidences are most satisfactorily interpreted as indicating that biphenyl is non-coplanar in the liquid or gaseous state while in the crystalline state it is maintained in the coplanar configuration presumably by the lattice force which overcomes the steric interference between the ortho hydrogen atoms. Then, the spectrum of biphenyl in the crystalline state should be that of the molecule in the coplanar configuration and the spectrum of biphenyl in the liquid or gaseous state should be that of the molecule in then on-coplanar configuration. Actually, in accordance with expectation, the spectrum of the crystal[11,12] is considerably different from that of the liquid or solution, and the former has the characteristic band at considerably longer wave-lengths than the latter, while the spectrum of the vapor is similar to that of the liquid;[12] so, it may be possible to infer the spatial configurations of biphenyls from their absorption spectra.

Previously,[13] the present author has determined the quantitative relations between the degree of deviation from coplanarity of the molecular configuration and the wave-lengths of the absorption spectrum as well as the extent of conjugation for stilbenes, and showed that the absorption maximum is shifted toward shorter wave-lengths and that the resonance energy is reduced progressively with increasing angle of twist of the phenyl groups out of the plane of the ethylenic linkage. The subject of the present paper is to determine analogous relations for biphenyls and discuss the spatial configurations of biphenyl and some related compounds.

Calculations

The calculations follow a procedure quite similar to the previous one[13] for stilbenes, so only the outline is given. In the present case the exchange integral for the 1-1′ bond is denoted by $\alpha\beta$. The value of the parameter α should vary with the length of the 1-1′ bond and the degree of twist of the benzene rings from the coplanar position around the 1-1′ bond. Since the biphenyl molecule belongs to the symmetry group D_2, the secular equation for the determination of the twelve approximate molecular orbitals as linear combinations of $2p\pi$ atomic orbitals is factorized into the following four equations:

$$\begin{aligned} A_1,\ & x^4+\alpha x^3-5x^2-3\alpha x+4=0,\\ B_2,\ & x^4-\alpha x^3-5x^2+3\alpha x+4=0,\\ B_1,\ & x^2-1=0,\\ B_3,\ & x^2-1=0, \end{aligned}$$

where $x=W/\beta=(Q-E)/\beta$, Q, E, and β having their usual meanings[14]. The numerical values of x obtained by solving these equations for various values of α represent the heights of the energy levels in units of β of the molecule in the spatial configuration prescribed by the corresponding value of α. The levels belonging to A_1 and those to B_2 vary, and those to B_1 and those to B_3 do not vary with α. These are reduced to those of benzene when α is zero. The absorption band characteristic of biphenyls is ascribed to the electronic transition from the highest occupied level to the lowest vacant level. In Table I, the values of the energy difference ΔE between these two levels and values of the extra-resonance energy $R.E.$ for various values of α are recorded. It is seen that the value of ΔE becomes larger and that of $R.E.$ smaller with decreasing value of α.

Since the exchange integral can be taken to be approximately proportional to the overlap integral, the value of α is assumed to vary with the angle of twist and the lengh of the 1-1′ bond R according to the relation

$$\alpha=S(R)\cos\theta/S(1.39\text{Å}),$$

where $S(R)$ is the π-π overlap integral when the bond length is R, and 1.39Å is the bond length between the adjacent carbon atoms in benzene ring. The value of $S(R)$ can be obtained from Mulliken's Table.[15] The value of R is assumed to be determined for any value of θ by the relation

$$\{S(R)-S(1.54\text{Å})\}/\{S(1.48\text{Å})-S(1.54\text{Å})\}=S(\theta)/S(0^\circ)=\cos\theta,$$

where $S(\theta)$ is the π-π overlap integral for the angle of twist of θ and $S(0^\circ)$ is that for the angle of twist of 0° at the constant bond length, since the molecule of biphenyl in the crystalline state is coplanar and the length of the 1-1′ bond is 1.48Å according to the X-ray analysis,[1] and since consequently R will vary from 1.48Å, to 1.54Å, the length of the normal C-C single bond, as θ varies from 0° to 90°. Thus, the value of θ being given, the corresponding value of α is easily obtained, and then those of ΔE and $R.E.$ are also obtained according to Table I. When θ is zero and R is 1.48Å, namely, for the coplanar

11) E. Merkel and C. Wiegand, *Z. Naturforsch.*, **36**, 93 (1948).
12) A. R. Deb, *Ind. J. Phys.*, 305 (1953).
13) H. Suzuki, This Bulletin, **25**, 145 (1952).
14) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., (1944), p. 255.
15) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

TABLE I

α	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
$\Delta E(\beta)$	1.410	1.460	1.512	1.566	1.624	1.682	1.742	1.804	1.868	1.934	2
$R.E.(\beta)$	0.382	0.312	0.248	0.192	0.142	0.098	0.064	0.036	0.016	0.004	0

TABLE II

Compound	Solvent	$\lambda_{max.}$(Å)	$\varepsilon_{max.}$	$\Delta E(\beta)$	α	θ	R(Å)	$R.E.(\beta)$
Biphenyl (crystal)	——	2754[a]	——	1.482	0.858	0°	1.48	0.285
4,5-Methylene-9,10-dihydrophenanthrene	Ethanol	ca. 2720[b]	ca. 18500	1.502	0.819	16.5°	1.482	0.260
9,10-Dihydrophenanthrene	Hexane	2635[c]	18000	1.555	0.720	31.5°	1.489	0.203
2,7-Dihydro-3,4-5,6-dibenzoxepin	Hexane	2500[c]	16500	1.646	0.562	47°	1.499	0.125
2,7-Dihydro-3,4-5,6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide	Water	2480[c]	15000	1.660	0.538	49°	1.501	0.115
Biphenyl	Heptane	2475	19000	1.664	0.531	50°	1.501	0.112
o-Methylbiphenyl	Heptane	2350	10000	1.759	0.373	63°	1.513	0.056
o,*o*′-Dimethylbiphenyl	Ethanol	(ca. 2270)[d]	6800	1.825	0.267	70.5°	1.520	0.029

a, A.R. Deb, Reference (12). *b*, R.N. Jones, Reference (22).
c, G.H. Beaven et al., Reference (18). *d*, G.H. Beaven et al., Reference (23).

molecule of biphenyl in the crystalline state, α is 0.858 and ΔE is 1.482(β).

According to Deb,[12] the characteristic band in the spectrum of biphenyl in the liquid state is split up into two broad bands at 36306 cm^{-1} (2754 Å) and 37386 cm^{-1} (2675 Å) in the case of the solid at 30°C, and the band at 36306 cm^{-1} is presumed to be the intrinsic band (ν_0). Consequently, this band corresponds to ΔE of 1.482 β. On the other hand, the "center of gravity of singlets"[16] in the absorption spectrum of benzene, 48000 $cm.^{-1}$ corresponds to ΔE of 2β. Therefore, in order to correlate the position of the absorption maximum with the calculated energy difference ΔE, it is assumed that the former expressed in wave number changes linearly with respect to the change in the latter from 36306 cm^{-1} corresponding to $\Delta E=1.482\beta$ to 48000 cm^{-1} corresponding to $\Delta E=2\beta$. Thus, the position of the absorption maximum of the biphenyl-type compound in which the two benzene rings are twisted to any extent from the coplanar position is easily inferred. Conversely, when the position of the absorption maximum is known experimentally, the degree of deviation from coplanarity, θ, as well as the extent of conjugation, $R.E.$, can be computed.

In Table II, the results of such computations are summarized. It is, for simplification, assumed that the absorption spectrum depends solely on the spatial configuration of the biphenyl skeleton in the compounds, and other effects, for example, the comparatively small bathochromic effect of the alkyl substituent or of the alicyclic bridge, are ignored.

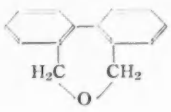
Discussion

As is seen from the Table II, the characteristic absorption maximum is shifted toward shorter wave-lengths and the extra-resonance energy is reduced progressively with an increasing angle of twist.

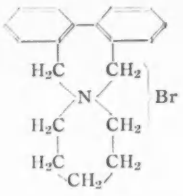
For biphenyl in solution, the angle between the two benzene rings has been computed to be 50°. According to the electron diffraction sector method study by Bastiansen,[3,17] the angle is found to be 45° ±10°, 52° ±10°, 54° ±5°, and 45° for biphenyl, 3, 3′-dichlorobenzidine, 3, 3′-dibromobiphenyl, and 3, 3′, 5, 5′-tetrabromobiphenyl respectively. If the actual angle is assumed to be the same for all the non-ortho-substituted biphenyls, it can be given the value 50° ±5° on the average.[17] The agreement between the value obtained here and that found by Bastiansen is surprisingly good, although the former refers to the molecule in solution while the latter to the molecule in the gaseous state. In this connection, the cases of the 2, 2′-bridged biphenyls are of interest. In these compounds the molecule is maintained in the comparatively rigid configuration. According to the models, the angle between the two benzene rings of the biphenyl skeleton in 2, 7-dihydro-3, 4-5, 6-dibenzoxepin (I) and 2, 7-dihydro-3, 4-5, 6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide (II) in which the 2, 2′-positions of biphenyl are bridged by a 7-membered ring is about 50°, and it is

16) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

17) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).



(I)



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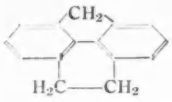

(III)

notable that these compounds show closely similar absorption spectra to that of biphenyl in solution,[18] and that the angle has been computed by the present method to be 47° and 49° respectively. This gives presumably some support to the above estimation of the angle of twist for the isolated molecule of biphenyl. Samoilov and Dyatkina,[19] in contrast to this, have deduced a value of about 30° for this angle in the isolated molecules of biphenyl and of terphenyl by calculations based on the molecular orbital method of the resonance energy and of the interaction between the nearest hydrogen atoms.

According to Beaven et al.,[18] the angle of twist in 9,10-dihydrophenanthrene in which the 2,2′-positions of biphenyl are bridged by a 6-membered ring is estimated to be about 20° from the model, while fluorene in which the 2,2′-positions of biphenyl is bridged by a 5-membered ring is best regarded as a strained planar structure. However, the absorption spectra of these two compounds are similar with the exception that in the latter compound fine structures appear.[20] The X-ray data, according to Jones,[21] favor a non-planar configuration for crystalline fluorene. On the other hand, in 4,5-methylene-9,10-dihydrophenanthrene (III), the conflicting steric requirements of the two bridges would appear to be most favorably compromised in an approximately planar configuration. The above estimations of the angle of twist seem to suggest that it is the case. Thus, this compound has the characteristic absorption band[22] at considerably longer wave-lengths than those of 9,10-dihydrophenanthrene and of fluorene and nearer to that of biphenyl in the crystalline state. This suggests presumably that the molecule of 4,5-methylene-9,10-dihydrophenanthrene is nearer to coplanar and that the molecule of fluorene as well as of 9,10-dihydrophenanthrene deviates from coplanarity to a larger extent as compared with 4,5-methylene-9,10-dihydrophenanthrene. It is doubtful, of course, whether much significance can be attached to the numerical values of the angle of twist shown in Table II especially for these 2,2′-bridged biphenyls, because the straining effects of the 2,2′-bridge linkages in these compounds would be too complicated to be treated by such a simple method. (The above assumption, for example, of the relation between R and θ may be not pertinent to these cases.)

The angle of twist for ortho-methylbiphenyl has been computed to be 63°, which is in best accord with the value 62° deduced from the model in which the length of the 1-1′ bond is 1.51 Å and an ortho hydrogen atom just touches the ortho methyl group.

It is notable that the spectrum of o,o'-dimethylbiphenyl is markedly different from that of o-methylbiphenyl. If the molecule of o,o'-dimethylbiphenyl assumed the trans form in which the ortho hydrogen atoms just contact with the ortho methyl groups, the configuration would be similar to that of o-methylbiphenyl, and consequently o,o'-dimethylbiphenyl would show a closely similar spectrum to that of o-methylbiphenyl. As a matter of fact, the spectrum of o,o'-dimethylbiphenyl has no distinct band; however, according to Beaven et al.,[23] it has the inflection at about 2270 Å, which is regarded as a vestigial conjugation band. When this value is taken as a basis for calculation, θ and R are computed to be 70.5° and 1.520 Å. These values are in good agreement with the corresponding values, 70.6° and 1.525 Å, found for 2,2′-dimethylbenzidine dihydrochloride by the X-ray crystal analysis.[24] Considering the fact that the value of the angle between the two benzen rings found for gaseous 2,2′-dichlorobiphenyl by the electron diffraction method,[17] 74°, and that found for crystalline

18) G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, **1952**, 854.
19) S. Samoilov and M. Dyatkina, *Zhur. Fiz. Khim.*, **22**, 1294 (1948); *Chem. Abst.*, **43**, 2606.
20) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).
21) Reference (22); Iball, *Z. Krist.*, **94**, 397 (1936); Cook and Iball, *Chemistry and Industry*, **55**, 467 (1936).
22) R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941).
23) G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner, and (in part) G. R. Bird, *J. Chem. Soc.*, **1954**, 131.
24) F. Fowwether and A. Hargreaves, *Acta Cryst.*, **3**, 81 (1950); *Chem. Abst.*, **44**, 7118; A. Hargreaves and W. H. Taylor, *J. Sci. Instruments*, **18**, 138 (1941); *Chem. Abst.*, **35**, 7261.

2, 2′-dichlorobenzidine by the X-ray investigation,[25] 72°, are in fact the same within the limits of experimental errors, and that both these compounds have been found to have the structures more similar to the *cis* form than to the *trans* form, it may be not unreasonable to compare the values for 2, 2′-dimethylbiphenyl in solution with those for 2, 2′-dimethylbenzidine dihydrochloride in the crystalline state, and to infer that the preferred configuration of the former as revealed by its absorption spectrum is similar to the configuration of the latter, which has been found to have the two ortho methyl groups in the *cis*-disposition.[24] At any rate, it seems to be sure that the conjugation between the two benzene rings still occurs, though faintly, in spite of large deviation from the coplanarity of the molecule. In this connection, it is of interest that Theilacker and Ozegowski[26] have found that 2, 2′-dimethyl-4, 4′-bis-(diphenylmethyl)-biphenyl has properties as a true biradical, although their results do not seem to be entirely free from ambiguity. Theilacker[27] mentioned also that the angle of twist was 37°–48° in this compound. In view of the above results, this value is presumably too small.

Lastly, it should be mentioned that the values computed above do not necessarily refer to the rigid configurations of the molecules but to the average or most probable ones. The fairly good agreements of the values computed above with the available data obtained by other methods throughout the cases under discussion may be supposed to prove the validity of such approximate treatments, and further, it is believed that the quantitative relations between the spatial configuration and the absorption spectrum as well as the extent of conjugation for biphenyl-type compounds have been almost satisfactorily determined here.

25) D. L. Smare, *Acta Cryst.*, **1**, 150 (1948); *Chem. Abst.*, **42**, 8045.
26) W. Theilacker and W. Ozegowski, *Ber.*, **73**, 33 (1940).
27) W. Theilacker, *Naturwiss.*, **31**, 505 (1943); *Chem. Abst.*, **38**, 3385.

Experimental

o-Methylbiphenyl was prepared after the Gomberg's procedure[28] by diazotizing *o*-toluidine in concentrated hydrochloric acid and adding the reaction mixture into a stirred mixture of sodium hydroxide solution and benzene. *o*, *o*′-Dimethylbiphenyl was prepared by the action of zinc dust on the diazotized *o*-toluidine in aqueous sulfuric acid solution to which ethanol was added, following the Gattermann's procedure[29] for preparation of biphenyl.

The measurements of the ultraviolet absorption spectra of biphenyl, *o*-methylbiphenyl, and *o*, *o*′-dimethylbiphenyl were carried out with a Beckman Quartz Spectrophotometer Model DU. As the solvent *n*-heptane was used. The concentration of the solutions was $1/3\times10^{-4}$ mole per liter for biphenyl and $1/2\times10^{-4}$ mole per liter for *o*-methylbiphenyl and for *o*, *o*′-dimethylbiphenyl.

Summary

The quantitative relations between the degree of deviation from coplanarity of the molecular configuration and the ultraviolet absorption spectrum as well as the extent of conjugation for the biphenyl-type compounds have been determined by calculations based on the molecular orbital method. On the basis of the results, the spatial configurations of biphenyl, *o*-methylbiphenyl, *o*, *o*′-dimethylbiphenyl, fluorene, 9, 10-dihydrophenanthrene, 4, 5-methylene-9, 10-dihydrophenanthrene, 2, 7-dihydro-3, 4-5, 6-dibenzoxepin, and 2, 7-dihydro-3, 4-5, 6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide have been discussed.

The author expresses his sincere thanks to Prof. Osamu Simamura, Drs. Saburo Nagakura, Makoto Takahashi, and Fujio Iimura for their kind guidance and encouragement throughout this study. Thanks are also due to the Ministry of Education for a Grant-in Aid for Scientific Research.

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28) M. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.*, **48**, 1372 (1926).
29) L. Gattermann, *Ber.*, **23**, 1226 (1890).

Vat Dyes of Acenaphthene Series. VI. Derivatives of Acenaphthene Violet[1]

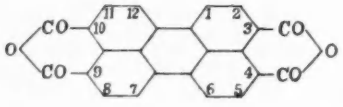
By Toshio MAKI and Harukichi HASHIMOTO

(Received July 1, 1954)

The formation of Acenaphthene Violet (II), a new, deep violet vat dye of maximum fastness, from 3,4,9,10-perylene-tetracarboxylic anhydride (I) and *o*-phenylenediamine was reported in our previous paper[2].

We have now prepared *p,p'*-dichloro derivative of Acenaphthene Violet (III), a brilliant violet vat dye, by condensation of 4-chloro-1,2-phenylenediamine (VII) with (I) at 170°, and also a violet blue dibenzo derivative (V) from (I) and 1,2-naphthylenediamine (VIII) at 150°. As 4-methoxy-1,2-phenylenediamine has been found to be unstable, di(*p*-methoxy-*o*-nitro)phenyl-diimide (VI) was synthesized by condensing 4-methoxy-2-nitroaniline (IX) and (I) at 200°, and *p,p'*-dimethoxy Acenaphthene Violet (IV) was obtained by its reduction with sodium sulfide via the corresponding diamino-dimethoxyl compound.

The fastness of the cotton dyeings of these vat dyes are excellent and among them the unsubstituted Acenaphthene Violet has the maximum light fastness, while the violet shade of the dichloro compound is most brilliant.

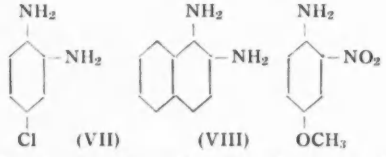


(I)

(II) X=H
(III) X=Cl
(IV) X=OCH_3

(V)

(VI)



Cl (VII) (VIII) OCH_3 (IX)

	Cotton dyeings		
	Shade	Light fastness	Yield of the theory (%)
Acenaphthene Violet (II)	Violet	8	60.6
Dichloro Derivative (III)	Brilliant violet	7~8	66.3
Dimethoxyl Derivative (IV)	Reddish violet	6~7	49.6
Dibenzo Derivative (V)	Violet blue	7	33.5

1) Read before the 7th Annual Meeting of the Chemical Society of Japan on April 3, 1954.
2) This Bulletin, **25**, 411 (1952).

Constitution		(II)	(III)	(IV)	(V)
Trichromatic coefficient	x	0.2712	0.2632	0.2794	0.2463
	y	0.1963	0.1796	0.2093	0.2074
Brightness Y (%)		6.49	6.55	8.21	7.88
Dominant wavelength (mμ)		564.0c	564.6c	562.8c	461
Color purity (%)		40.8	46.2	37.4	38.1

More accurate comparison of the shades of Acenaphthene Violet and its derivatives were carried out using G.E. recording spectrophotometer with 1% cotton dyeings (IW method) and the obtained reflectance curves (Fig. 1) were analysed according to the I.C.I. system.

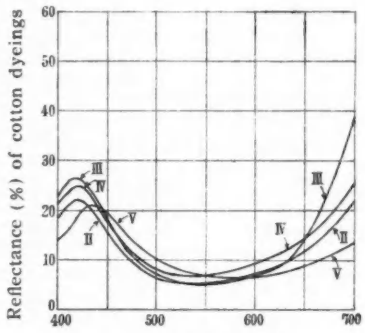


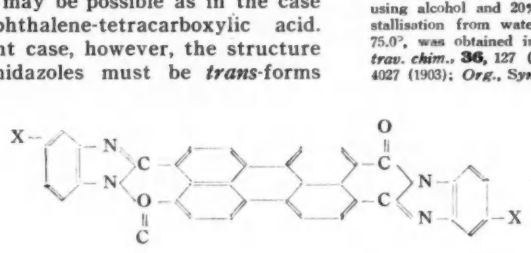
Fig. 1.

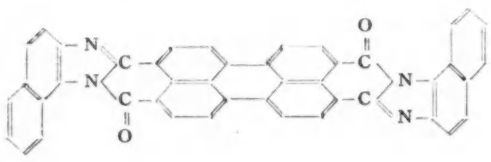
These vat dyes of the mono-imidazole type (II–V) are easily soluble in alkaline hydrosulfite and also soluble in 85~90% sulfuric acid. The straight and short conjugation between the two upper (3,10–) carbonyls is considered as the cause of the easy vattability. The associated bis-imidazoles (X–XI), violet blue or blue pigments of highest stability, are the ultimate reaction products and insoluble in alkaline hydrosulfite. Theoretically both *cis*- and *trans*-isomers of the bis-imidazoles may be possible as in the case of 1,4,5,8-naphthalene-tetracarboxylic acid. In the present case, however, the structure of the bis-imidazoles must be *trans*-forms (X–XI) of long and crooked conjugation between the two carbonyls (3,9–) owing to their perfect insolubility against alkaline hydrosulfite. The associated *o,o'*-diamino compounds, the initial condensation products, are insoluble in 85–90% sulfuric acid and have weak dyeing properties of low value.

Experimental Part

Dichloro Derivative of Acenaphthene Violet (III).—Perylene-tetracarboxylic anhydride (1, 31 g., 1 mol. ratio) was heated with an excess of 4-chloro-1,2-phenylenediamine[3] (4.8 g., 10 mol. ratio) and 1.0 g. (5 mol. ratio) of glacial acetic acid in an oil bath under reflux at 170° (bath temperature) for 1 hour. The product was heated up with 20 cc. of alcohol, the hot solution was filtered and washed with more alcohol until the filtrate became colorless. The collected precipitate was then treated with 200 cc. of hot aqueous 1% sodium hydroxide. The amount of the unchanged tetracarboxylic acid (alkali soluble) was only a trace. The yield of the crude condensation product was 1.92 g. The crude product was finely powdered, kept with 4 g. of sodium hydroxide, 4 g. of sodium hydrosulfite and 200 cc. of water at 50° for 15 minutes, filtered, and the insoluble part was further treated with 2 g. of sodium hydroxide and 2 g. of sodium hydrosulfite and 100 cc. of water. The part insoluble in the alkaline hydrosulfite, 0.26 g. or 12.9% of the theory, is the blue violet bis-imidazole pigment (X,X=Cl)

3) *p*-Chloroaniline was acetylated with acetic anhydride in benzene to *p*-chloroacetoanilide, m.p. 179.5—180.5° (corr.), in 94.7% yield, converted then into 4-chloro-2-nitroaniline, m.p. 116.4—116.9°, by nitration in conc. sulfuric acid, hydrolysis with 70% sulfuric acid and recrystallisation from water. Yield was 62.9%. The latter was reduced with zinc dust using alcohol and 20% sodium hydroxide and after recrystallisation from water 4-chloro-1,2-phenylenediamine, m.p. 75.0°, was obtained in 50.3% yield. See also Bruyn, *Rec. trav. chim.*, **36**, 127 (1916); Ullmann, Manthner, *Ber.*, **36**, 4027 (1903); *Org. Synth.*, **19**, 70 (1939).


(X)


(XI)

The combined vat filtrate was oxidized by a current of air, the collected precipitate, as a dry powder, dissolved in 42 g. of 99.2% sulfuric acid and 4.3 cc. of water was dropped in under ice cooling to produce 90% sulfuric acid. The insoluble, 0.08 g. or 3.7% of the theory, is the *o,o'*-diamino compound, which dyes cotton in weak, dull violet red of low value from a violet red vat (IW).

The part soluble in 90% sulfuric acid is the main dye, dichloro Acenaphthene Violet (III), the yield was 1.38 g. or 66.3% of the theory. The dichloro compound (III) is a black violet powder, soluble in conc. sulfuric acid and the solution shows blue (thin layer) and violet blue (thick layer) dichroism with weak red fluorescence. Violet precipitate resulted from the conc. sulfuric acid solution by the addition of water. Hydrosulfite vat (IW) is red violet and dyes cotton in brilliant violet of powerful intensity with 1~2% dye, a little more bluish than the chlorine free Acenaphthene Violet (II). The light fastness of the cotton dyeings were found to be 7—8 grade. Found Cl, 10.91; calcd. for $C_{36}H_{16}O_3N_4Cl_2$ (III): Cl, 11.37%.

Dimethoxyl Derivative of Acenaphthene Violet.—A mixture of 1.31 g. (1 mol. ratio) of perylene-tetracarboxylic anhydride and 7.8 g. (14 mol. ratio) of 4-methyoxy-2-nitroaniline (m.p. 124.5—125°, corr.)[4] was heated with 1.0 g. (5 mol. ratio) of glacial acetic acid in an oil bath under reflux at 200° (bath temperature) for 7 hours. The unchanged components were removed with 100 cc. of alcohol and 500 cc. of 1% sodium hydroxide as above. The yield of the dinitro compound (VI) was 1.60 g. or 69.3% of the theory. It is a dark brownish red crystalline powder with a pink streak, soluble in conc. sulfuric acid with violet blue (thin layer) and violet red (thick layer) dichroism without fluorescence. Pink precipitate is formed from the conc. sulfuric acid solution by the addition of water. It dyes cotton in a weak, dull violet red shade of diamino compound from a violet red vat (IW). The vat shows weak orange fluorescence. The powder is a little soluble in boiling nitrobenzene with red-orange color and strong green-yellow fluorescence.

The dinitro compound (1.30 g., 1 mol. ratio) was dissolved in 50 g. of ice cold conc. sulfuric acid and poured into 1,000 cc. of ice cold water. The filtered and neutral washed paste was reduced with 1.1 g. of 55% sodium sulfide (4 mol. ratio) and 15 cc. of water by treating 1 hour at room temperature and 3 hours at 60°. It was then made up to 100 cc. with warm water (60°), the collected precipitate washed neutral and dried at 110° for 5 hours. The yield of the crude product was 1.20 g.

The crude reduction product was treated with 4 g. of sodium hydroxide, 4 g. of sodium hydrosulfite and 200 cc. of water at 50° for 15 minutes. The amount of the hydrosulfite insoluble (dimethoxy bis-imidazole) was only a trace. The soluble part was, after air oxidation, separated with 55.6 parts of 85% sulfuric acid. The part insoluble in 85% sulfuric acid corresponds to the diamino compound (0.24 g. or 20.2% of the theory). It dissolves in conc. sulfuric acid with blue color (without dichroism) and weak red fluorescence, and red violet precipitate is produced from the solution by the addition of water. Hydrosulfite vat (IW) is violet red with weak orange fluorescence and dyes cotton in weak, dull violet red of low value.

The part soluble in 85% sulfuric acid is the main dye, dimethoxy Acenaphthene Violet (IV). It was precipitated by pouring the sulfuric acid filtrate into ice water. The yield was 0.83 g. or 71.6% of the theory (49.6% of the theory from 4-methoxy-2-nitroaniline). It is a dark violet powder with a violet streak. The conc. sulfuric acid solution is blue (without dichroism) with weak red fluorescence, from which a red violet precipitate is formed by water. It is very easily soluble in alkaline hydrosulfite (IW) giving red violet vat with weak orange fluorescence and dyes cotton in a deep reddish violet shade. The grade of the light fastness of its dyeings is 6—7. The substance is a little soluble in boiling nitrobenzene with violet red color and green yellow fluorescence. Found: N, 8.93; calcd. for $C_{38}H_{22}O_5N_4$ (IV): N, 9.12%.

It is interesting that in the case of this methoxyl compound the imidazolization of one of the *o*-amino groups occurs readily at the same time with sodium sulfide reduction even at 60°. When the reduction was carried out at 100° for 3 hours the imidazolization proceeded further, giving 36% of the bis-imidazole pigment (X, X=OCH_3), 16% of the *o,o'*-diamino compound and only 32% of the mono-imidazole dye (IV). The drying temperatures of the products, when they were not higher than 110°, had practically no influence upon the rate of imidazolization.

Dibenzo Derivative of Acenaphthene Violet (V).—Perylene-tetracarboxylic anhydride (1.31 g., 1 mol. ratio) was heated with 5.2 g. (10 mol. ratio) of 1,2-naphthylenediamine (m.p. 95—96°, uncorr.)[5] and 1.0 g. (5 mol. ratio) of glacial acetic acid in an oil bath at 150° (bath temperature) for 1 hour and the unchanged components were removed with alcohol and 1% sodium hydroxide as in the above experiments. The weight of the crude condensation product was 2.10 g. It was then treated twice with 4 g. of sodium hydroxide, 4 g. of hydrosulfite and 200 cc. of water at 50° for 15 minutes and filtered. The amount of the hydrosulfite insoluble was 1.16 g. or 55.3% of the crude product. The part soluble in hydrosulfite was treated, after air oxidation as a dry powder, with 90% sulfuric acid. The amount of the sulfuric

4) *Org. Synth.*, **25**, 78 (1945); 4-Methoxy-2-nitroacetanilide, m.p. 118.7—119.2° (corr.) was obtained in 73.5% yield from *p*-anisidine and then saponified with potassium hydroxide in methanol to 4-methoxy-2-nitroaniline. The yield was 99.3%.

5) Diazotized aniline was coupled with *β*-naphthylamine in alcoholic solution to 1-benzene-azo-2-naphthylamine, m.p. 102.5—103° in 90.8% yield of the theory. It was then reduced with zinc dust in aqueous acetic acid. The yield of pure 1,2-naphthylenediamine was 53.2%. See Bamberger, Schieffelin, *Ber.*, **22**, 1376 (1889); Yokote et al., *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 476 (1951).

acid insoluble was a trace and the soluble part was the main vat dye, dibenzo Acenaphthene Violet (V), which was collected after pouring the sulfuric acid filtrate into ice water. The yield was 0.74 g. or 33.5% of the theory[6]. It is a black violet powder of violet streak, hardly soluble in organic solvents, soluble in conc. sulfuric acid blue without dichroism and fluorescence and a violet precipitate is formed from the solution by the addition of water. The hydrosulfite vat (IW) is red violet, from which cotton is dyed in a violet blue (navy blue) shade of excellent light fastness (grade 7). Found: N, 8.24; calcd. for $C_{44}H_{22}O_3N_4$ (V): N, 8.56%.

The *o,o'*-diamino compounds of the benzene series (N,N'-diphenyldiimide type) were soluble in alkaline hydrosulfite, but the hydrosulfite insoluble of the above 150°-condensation product of 1,2-naphthylenediamine was found to be mainly *o,o'*-diamino compound by the actual estimation of the nitrogen evolution from the corresponding diazo compound. The di(*o*-amino)naphthyl-diimide is soluble in conc. sulfuric acid in blue color without dichroism and fluorescence and is a violet substance in the precipitated state. The hydrosulfite insoluble of 120°-condensation was also the *o,o'*-diamino compound. On the other hand, however, the hydrosulfite insoluble of 170°-condensation was mainly the bis-naphthoimidazole, which had analytically no more free $-NH_2$ groups. The bis-naphthoimidazole (XI) is a blue pigment and its blue conc. sulfuric acid solution shows neither dichroism nor fluorescence.

6) By 170°-condensation the yield of the main vat dye (V) was 17.4% and at 120° 16.5% of the theory.

The authors express their gratitude to The Government Industrial Research Institute, Tokyo for the measurement of reflectance curves using G.E. recording spectrophotometer.

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*The Crystal Structure of Diallylsilanediol**

By Nobutami KASAI and Masao KAKUDO

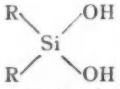
(Received July 17, 1954)

Introduction

The present study is the fourth in a series of organosilanol crystal structure determinations carried out in this laboratory, the previous three compounds examined having been diethylsilanediol[1,2,3], diphenylsilanediol[4], and bis-dimethylhydroxysilyl methane[5].

Diallylsilanediol, $(CH_2=CH\text{-}CH_2)_2Si(OH)_2$, was first prepared by Mr. R. Ōkawara and his coworkers[6].

This compound was selected for study as a typical one of the unsaturated dialkylsilanediols having the formula



It is of interest to compare the structure of this crystal, with the cases of the above-mentioned compounds especially, in respect to the molecular chain formation through hydrogen bondings or the layer structure.

Experimental

The crystals used in this experiment were recrystallized from their ethyl ether-petroleum ether solution. The crystals are colorless, flat prismatic in habit as shown in Fig. 1; the c-face is a remarkably complete cleavage plane. These properties are quite similar to those of diethylsilanediol. It is well dissolved in oxygen containing organic solvents.

Melting point: 81±0.5°C.

Density: 1.105 (by floatation method at 10°C)

For the structure determination, the oscillation and the rotation photographs were taken around both the b-axis and a-axis using nickel filtered CuK_α radiation.

Some physical constants and the dimensions of

* Read before the 7th annual meeting of the Chemical Society of Japan held in Tokyo, April, 1954.

1) M. Kakudo and T. Watase, *Technol. Repts. Osaka Univ.*, **2**, 50 (1952).

2) M. Kakudo and T. Watase, *J. Chem. Phys.*, **21**, 167 (1953).

3) M. Kakudo, N. Kasai and T. Watase, *J. Chem. Phys.*, **21**, 1894 (1953).

4) T. Watase, M. Kakudo and N. Kasai *Ann. Repts. Textile Research Inst. Osaka Univ.*, **6**, 38 (1952) (in Japanese).

5) M. Kakudo and T. Watase, *Ann. Repts. Textile Research Inst. Osaka Univ.*, **7**, 17 (1953) (in Japanese).

6) R. Okawara, K. Hashitani, and T. Watase, This Bulletin, **26**, 279 (1953).

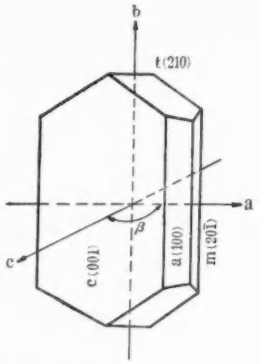


Fig. 1. The crystal form

the unit cell were listed in Table I in comparison with those of diethylsilanediol.

TABLE I

	Diallylsilanediol	Diethylsilanediol
m.p.	81±0.5°C	96±0.5°C
Density	1.105	1.134
System	Monoclinic	Monoclinic
Cleavage	(001)	(001)
Unit cell	a=14.59 kX.	a=14.55 kX.
	b= 4.94 kX.	b= 4.96 kX.
	c=13.37 kX.	c=10.25 kX.
	β=114°30′	β=110°50′
Space group	C^5_{2h}	C^5_{2h}

The physical and chemical properties of these two silanols suggest that they are much like each other not only in their chemical constitution but also in crystal structure.

The unit cell contains four molecules of $(CH_2=CH\text{-}CH_2)_2Si(OH)_2$ (calculated value z=4.03).

All the reflexions (hkl) were observed without any speciality, whereas no reflexions (h0l) with h odd or (0k0) with k odd were found. Consequently, the space group corresponds to C^5_{2h}—$P2_1/a$. All the atoms of this molecule are to be in the general positions of C^5_{2h}.

$$(x,\ y,\ z)\ (\bar{x},\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z)\ (x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z)\ (\bar{x},\ y,\ z).$$

The relative intensities of reflexions were estimated by visual method with the standard density scale. The observed structure factors, $|F_{obs.}|$'s, were derived from these values by the usual method.

The Patterson function was first calculated using $F^2_{obs.}$'s. Approximate atomic arrangement was easily assumed from the b-plane projection of Patterson function by comparing with that of diethylsilanediol.

After several trials of structure factor and electron density computations, a good agreement between $F_{obs.}$ and $F_{calc.}$ was obtained for both of F(h0l)'s and F(0kl)'s. The final electron density map is shown in Fig. 2. The atomic parameters

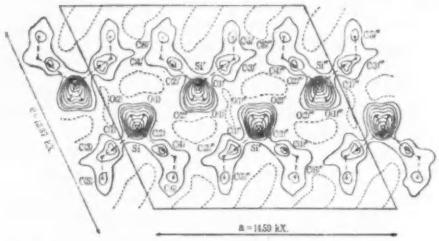


Fig. 2a. The Fourier projection map on the b-plane.

are given in Table II. The observed and calculated F-values are also listed in Table III. The

TABLE II

ATOMIC PARAMETERS

	x	y	z
O(1)	0.084	0.257	0.463
O(2)	0.138	$\bar{0}.257$	0.463
Si	0.082	0.000	0.386
C(1)	$\bar{0}.054$	0.091	0.296
C(2)	0.146	$\bar{0}.091$	0.296
C(3)	$\bar{0}.115$	0.171	0.259
C(4)	0.182	$\bar{0}.171$	0.259
C(5)	$\bar{0}.152$	0.244	0.153
C(6)	0.138	0.244	0.153

TABLE III

A PART OF CALCULATED AND OBSERVED F-VALUES

(hkl)	$F_{obs.}$	$F_{calc.}$	(hkl)	$F_{obs.}$	$F_{calc.}$	(hkl)	$F_{obs.}$	$F_{calc.}$
001	86	−87	20$\bar{7}$	—	2.2	60$\bar{1}$	28	35
002	36	−27	20$\bar{8}$	11	−1.6	60$\bar{2}$	6	−15
003	30	−18	20$\bar{9}$	—	−11	60$\bar{3}$	30	−34
004	8.0	7.2	400	116	−108	60$\bar{4}$	19	29
005	29	−10	401	36	44	60$\bar{5}$	27	−38
006	25	8.3	402	22	17	60$\bar{6}$	38	40
007	—	11	403	46	−35	60$\bar{7}$	—	−10
008	41	28	404	37	28	60$\bar{8}$	31	−16
009	13	−46	405	20	25	60$\bar{9}$	40	25
0.0.10	25	−11	406	18	−33	800	25	−7.5
200	38	30	40$\bar{1}$	19	24	801	53	32

201	88	−74	$40\bar{2}$	20	−22	802	38	16
202	91	72	$40\bar{3}$	104	108	803	17	13
203	57	−40	$40\bar{4}$	52	−46	$80\bar{1}$	9	7
204	27	24	$40\bar{5}$	17	−22	$80\bar{2}$	9	27
205	18	− 7	$40\bar{6}$	41	38	$80\bar{3}$	51	−71
206	—	2.5	$40\bar{7}$	29	−34	$80\bar{4}$	15	31
207	—	4.5	$40\bar{8}$	15	−21	$80\bar{5}$	10	9
208	19	22	$40\bar{9}$	24	35	$80\bar{6}$	15	−17
$20\bar{1}$	8.3	8.2	600	25	−27	$80\bar{7}$	35	22
$20\bar{2}$	56	−53	601	57	51	$80\bar{8}$	21	−18
$20\bar{3}$	117	80	602	34	−27	$10.0.\bar{1}$	27	−34
$20\bar{4}$	77	53	603	33	− 8	$10.0.\bar{2}$	46	46
$20\bar{5}$	28	33	604	30	20	$10.0.\bar{3}$	—	1.3
$20\bar{6}$	20	−17						

values of $R=\sum||F_o|-|F_c||/\sum|F_o|$ is 0.27 for (h0l) and 0.33 for (0kl) respectively. Calculated structure factors have been corrected for atomic thermal motion by the factor $\exp\{-B(\sin\theta/\lambda)^2\}$ with $B=4.0\times10^{-16}$.

The (F_o-F_c) series map (Fig. 3) indicates,

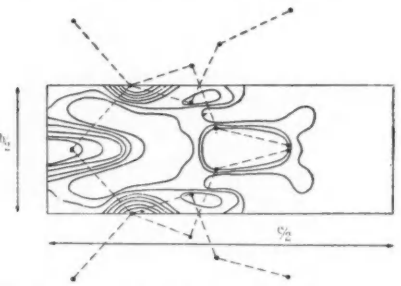


Fig. 2b. The Fourier projection map on the a-plane.

though it may not be said to be accurate, the positions of hydrogen atoms such as are assumed from its molecular structure.

Interatomic distances and bond angles are given in Table IV.

TABLE IV

INTERATOMIC DISTANCES AND BOND ANGLES

(The suffix and number of each atom are the same as in Fig. 2 or Fig. 4.)

Si—0(1)=1.63 Å.,	∠0(1)–Si–0(2)=110°,
Si—C(1)=1.90 Å.,	∠C(1)–Si–C(2)=110°,
C(1)—C(3)=1.54 Å.,	∠Si–C(1)–C(3)=109°,
C(3)—C(5)=1.33 Å.,	∠C(1)–C(3)–C(5)=120°,
C(6)...C(5)''=3.93 Å.,	0(1)'*...0(2)'=2.53 Å.,
C(6)...C(5)'''*=4.16 Å.,	0(1)'*...0(2)=3.75 Å.,
C(6)...C)6)'''*=4.25 Å.,	0(1)'*...0(2)''=3.75 Å.,
C(5)''...C(5)'''*=4.53 Å.,	0(1)'*...0(1)''=3.65 Å.,
C(5)''...C(6)'*=4.16 Å.,	0(1)'*...0(1)''*=3.65 Å.

Discussion

The silicon-tetrahedron was recognized as retaining its ordinary shape and size.

The feature of the whole structure is considerably similar to that of diethylsilanediol as shown in Fig. 4.

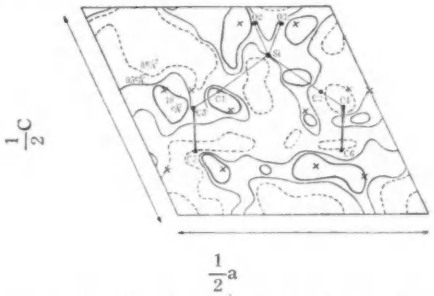
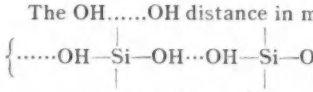


Fig. 3. (F_o-F_c) series map. (The projection on the b-plane)
×: the assumed position of the hydrogen atom.

The OH.....OH distance in molecular chains



parallel to the b-axis is 2.53 Å (2.54 Å in diethylsilanediol). These OH...OH linkages by hydrogen bonds join the molecules to form infinite chains parallel to the b-axis just the same as in the case of diethylsilanediol.

The molecular chains are arranged parallel to each other in a plane (c-plane), and these sheets construct the layer structure, allyl groups of neighbouring molecules contacting back to back as in Fig. 4a. The remarkable

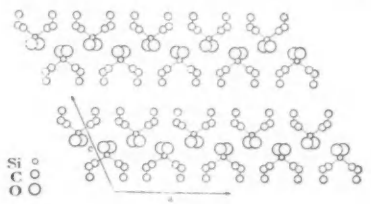


Fig. 4a. The atomic arrangement projected on the b-plane.

cleavage of (001) will be sufficiently understood from such a layer structure.

The feature of approach of OH-groups around an OH-group (Fig. 4b), and interaction

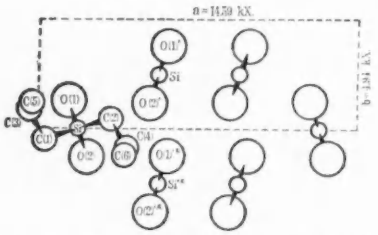


Fig. 4b. The arrangement of hydroxyl groups. (The projection on the plane $Z=\frac{1}{2}$, allyl groups are omitted except two.)

of allyl groups will be explained by the same argument as presented on diethylsilanediol. This structural similarity is to be recognized as an example of isomorphism for the chemical homologues of diorganosilanediols.

The most remarkable result is the fact that the molecular cohesion in the crystal of diorganosilanediol is mainly due to the hydroxyl bond which was formed along the b-axis by strongly polarized OH-groups, and such a way of molecular association characterizes the whole feature of crystal structure of each diorganosilanediol, which we have dealt with.

From the spreading of peaks about carbon atoms in the electron density maps and about hydrogen atoms in the (F_o-F_c) series, it is reasonably supposed that the thermal motion of allyl groups in the crystal may be in a considerable degree. This thermal libration is a noticeable property of the organoradicals directly combined to silicon atom as indicated in many other works. The low interaction of allyl groups, plus the long distance of Si-C bond should bring about a weak barrier to their thermal motion.

It is interesting to note that the peaks for all atoms in the electron-density map of Fig. 2b are elongated in such a manner as to suggest that one of the principal thermal motions is a vibration of the entire molecule along the direction perpendicular to the c-plane. This fact is also in agreement with our consideration that the intermolecular cohesive force of this crystal may be comparatively weak in this direction.

However, the anomaly of (001) reflexions expected to be sensitively influenced by such motion was not observed appreciably, though there were observed a few diffuse Laue spots. The qualitative relation of these diffuse reflexions and the molecular motion will be explained in comparison with diethylsilanediol before long.

Conclusion

The morphology and the crystal structure of diallylsilanediol were presented.

The whole feature of this structure is nearly the same as that of diethylsilanediol previously studied by one of the authors.

Many of the chemical and physical properties of diorganosilanediols can be interpreted in terms of obtained structural principles.

It was verified that the chemical homologues of diorganosilanediols give rise to a structural isomorphism.

The OH...OH distance (2.53 Å) with hydrogen bond is the same as in the case of diethylsilanediol (2.54 Å) within the range of error.

The thermal motion of allyl groups combined to silicon atom is considered as more vigorous than that in the corresponding organic compounds even at room temperature.

The authors wish to express their sincere thanks to Mr. R. Ōkawara who kindly gave them some precious samples.

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*The Alternating Current Polarisation with Respect to Hetero-Pair Electrodes**

By Shigeo NAGAURA and Kazuo SASAKI

(Received July 19, 1954)

Introduction

It was long ago when the galvanic polarisation such as the polarisation capacitance and the polarisation resistance, caused by alternating current, came into our knowledge.

As was shown in some reviews made recently by one of the present authors[1] and also by Shaw and Remick[2], many investigators have been concerned with the problem either theoretically or experimentally for the past 70 years or more.

In spite of the fact that the theoretical treatments were carried out in detail from the various standpoints, the experimental investigations did not give us any satisfactory explanation for the nature of the polarisation effect. One of the causes of the present meagre experimental knowledge is the difficulty of the measurement of this sort. Above all it is serious that exact reproducibility can never be attained. In fact, all the investigators have stated that the observed values change, not only from one sample of the liquid to another, or from one set of the electrodes to another, but also change with time for the same set of electrodes and the same sample of liquid.

Here we want to verify a fundamental character of polarisation effect, caused by the application of alternating current, which has been assumed tacitly by prior investigators. In other words, our main subject is to know whether the polarisation characters, measured as to a whole cell, can be attributed to each single electrode or not.

No such attempt has been made so far as we aware.

Robertson[3] attempted to determine the polarisation capacitance for a single platinum electrode immersed in hydrochloric acid solution, along the line indicated by Grahame[4] for dropping mercury electrode.

Though his experiments were carried out also for the polarisation capacitance of the single electrode of solid metal, the effect observed was essentially the direct current polarisation, in which the steady state may be reached, We are going to study the problem in a different way.

Experimental

The measuring devices consist of an ordinary impedance bridge and an audio frequency generator. The latter was made in our laboratory. The frequency was kept at 1440 cycles per second, which was corrected with a standard oscillator. A variable air condenser attached to the balancing arm of the bridge changes in its capacity from 1.11μF. to 0.0001μF.

Since the principal purpose of this experiment was the attribution of the polarisation characters to each component electrode (electrode/soln. interface), several kinds of metals were prepared for electrode materials, each having the same dimension, that is, the disk plate having 2 cm. in its diameter. Metals prepared were Pt, Ni, Cu and Ag. Copper electrode was electropolished before each measurement. Nickel and silver electrodes were prepared by means of electroplating on the copper surface. The solutions investigated were N/100, N/10 and 1N KCl aqueous solution. Alcoholic solutions of KCl in two different concentrations were also investigated. One of these alcoholic solutions was made in the following way: 2 cc. of 1N KCl aqueous solution was dropped into 1 litre of 96% ethyl alcohol and after vigorous shaking the bottle was kept still at 0°C for a day, then the excess precipitation of potassium chloride was separated by careful decantation. A portion of the saturated solution, thus obtained, was diluted by ninefold amount of ethyl alcohol.

Measurements were carried out at 28°C and at 0°C, the former temperature was obtained by means of well regulated thermostat and the latter was kept by means of ice-water mixture.

Figure 1a shows the conductivity cell which is made of Telex glass and has been used for all of the experiments. As is clearly seen, from the figure, both of the two electrodes are allowed to move so as to be able to determine the polarisation resistance in such a way as will be explained in the following article.*

* The terms homo-pair electrodes and hetero-pair electrodes are defined as a set of electrodes consisting of the same or different metals, respectively.

1) S. Nagaura, *J. Electrochem. Soc. Japan*, **19**, 249 (1951).
2) M. Shaw and A. Remick, *J. Electrochem. Soc.*, **97**, 324 (1950).
3) W. Robertson, *J. Electrochem. Soc.*, **100**, 195 (1953).
4) D. C. Grahame, *J. Am. Chem. Soc.*, **68**, 301 (1946); *Chem. Revs.*, **41** 441 (1947).

A Short Explanation of the Equivalent Series Circuit

Though most investigators have treated their measured quantities of the polarisation phenomena using the equivalent series circuit, no serious discrepancy has appeared in such treatment.

Warburg first suggested and developed the idea that the diffusion is responsible for the incomplete reversibility of the electrode reactions. By the integration of Fick's law of diffusion with suitable boundary conditions he reached the conclusion that polarisation causes a capacitance in series with the resistance of the electrolyte. His theory has been extended by many authors thereafter, but owing to their different viewpoints, there exist several kinds of equivalent circuits for an electrolytic cell (See Ref. 1). Some of them, however, can not be adopted practically because of the complexity of their circuit elements.

Kohlrausch first found that the inverse electromotive force, Ep, caused by polarisation, is proportional to the amount of electricity passed through the cell, i.e.,

$$Ep=1/C\int Idt. \tag{1}$$

If the current, I,is alternative and expressed as $I=Io\ \sin\omega t$, Eq. 1 then becomes

$$Ep=Io/\omega C\ \sin(\omega t-\pi/2). \tag{2}$$

This means that Ep is equal to the voltage drop which occurs when a.c., $I=Io\ \sin\omega t$, passes through a condenser of capacity C.

Wien suggested that the formula on Ep must have a term with regard to the phase difference, φ, i.e.,

$$Ep=Io/\omega C\ \sin\left\{\omega t-(\pi/2-\varphi)\right\}. \tag{3}$$

This equation means that Ep is equal to the voltage drop which occurs when a.c. is applied to a series circuit consisting of a condenser of capacity $C/\cos\varphi$ and a resistor of resistance $\sin\varphi/\omega C$.

Figure 2a is a schematic expression of the equation 3.

In this work we assume the identical behavior of the two electrodes, thus the equivalent circuit can be expressed as in Fig. 2b.**

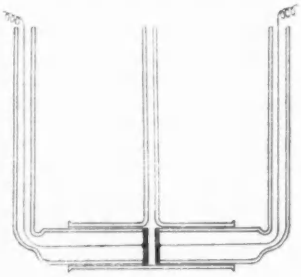

Fig. 1 a. Conductivity cell

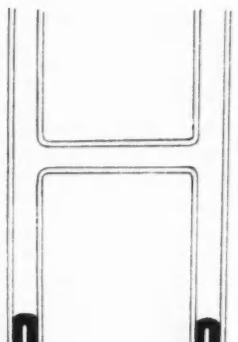

Fig. 1 b. H-Form electrode

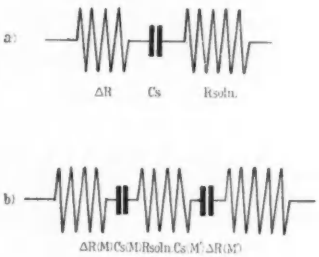

Fig. 2a. Equivalent circuit

Results and Discussion

Reproducibility of the Measurements.—At first, the effect of the immersion time and the reproducibility of the measurements were detected.

Shaw and Remick reported that when the platinum electrodes are combined together electrically and used as the anode for the electrolysis of alkaline cyanide solution before each conductivity measurement, reproducible results were obtained. As far as we repeated their experiment, however, the satisfactory agreement with them was not recognised. Moreover the systematic influence of the electrolysis was not observed. This is shown in Table 1. In Table 1, Rp and Cp are the values of bridge readings and Rs and Cs are of those converted into series circuit, respectively.

From the Table we can not see any regenerative effect of the electrolysis. (Some atten-

TABLE I.*

	$Rp(\Omega)$	$Cp(\mu F.)$	$Rs(\Omega)$	$Cs(\mu F.)$
1) Anodic treatment; 15 min..				
Immersion time (min.)				
0	711	0.1051	48.7	3.33
80	628	0.0914	49.4	4.27
220	619	0.0884	49.6	44.4
2) Anodic treatment; one hour.				
0	615	0.0899	49.1	4.45
3) Anodic treatment; 12 min..				
0	760	0.1063	49.3	3.03
10	752	0.1059	49.7	3.11
50	757	0.1068	49.1	3.04
105	762	0.1079	48.8	3.03
4) Anodic treatment; 20 min..				
0	789	0.1068	49.3	2.71
20	775	0.1059	49.5	2.71
50	776	0.1080	49.4	2.58

* The values are arranged in order of the measurements.

It is seen from the table that the values do not depend on the time of anodic treatment but on the immersion time.

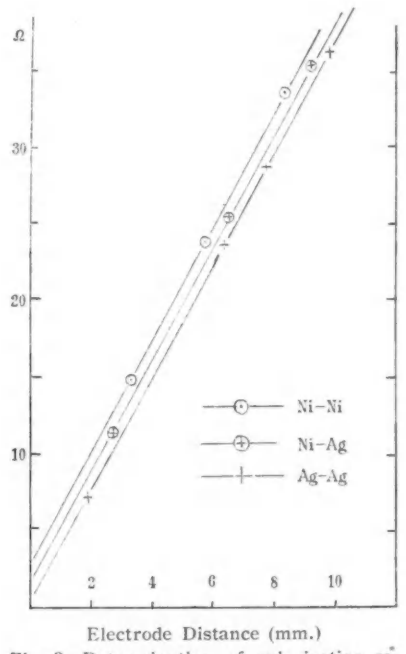

Fig. 3 Determination of polarisation resistance

tion must be given to zero minute values.)

These observations were made by H-form platinum electrodes, which are shown in Fig. 1b, in a wide porcelain bath at room temperature.

Shaw and Remick also stated the effects of immersion as follows:

1) The electrodes were immersed for one hour before taking a reading. Then they were removed from the measuring solution and washed with hot water just before boiling. Finally, the electrodes were returned to the cell and *Cs* was immediately determined. The result was the same to "one hour value".

2) The changes of *Cs* with time, whatever their nature, were essentially independent of any application of the current.

These results were in agreement mostly with our trace experiment.

In consequence, we conclude that the "aging process" of the electrodes makes it impossible to determine the absolute values of the polarisation impedances for all the individual electrode, owing to the incomplete reversibility of the a.c. electrode reactions, and special precautions have to be taken even to obtain relative values which are comparable.

A similar opinion was reported by jaffé and Rider[5] recently. In this connection, Jones and Christian[6] reported that their *Cs* value with silver electrodes was greater than that for platinum, while Wien had obtained the contrary results. Thus it is also doubtful whether it is possible to determine the order of the *Cs* values of various metals. From the above arguements, it must be said that absolute order can not be obtained in practice, owing to instability of each metal surface against the action of alternating current and this inability is not because of the experimental mistake.

Thus in the following experiments we took

5) G. Jaffé and A. Rider, *J. Chem. Phys.*, **20**, 1077 (1952).
6) G. Jones and S. Christian, *J. Am. Chem. Soc.*, **57**, 272 (1935).

great care to get reliable data; we need the data only for comparison. In other words, a series of experiments should be completed without delaying.

Additivity of the Polarisation Characters with Respect to a Single Electrode.—Since the arrangement of the balancing arm of the bridge is in parallel, impedances of each element of Fig. 2a is easily calculated by the following relations;

$$Rs = Rt + \Delta R = n(Rp/1 + \omega^2 Cp^2 Rp^2) \quad (4)$$

$$Cs = 1/n \cdot Cp(1 + 1/\omega^2 Cp^2 Rp^2) \quad (5)$$

where n is the arm ratio of the bridge, and suffixes s and p are taken to mean the series and parallel values, respectively.

As far as we deal with the homo-pair measurements, these series values are easily divided into two parts corresponding to each metal/soln. interface. The values for hetero-pair electrodes may be calculated from the values of homo-pair measurements and also by direct measurements. The results thus obtained for aqueous KCl solutions are tabulated in Table II. Values in Table III are those for KCl saturated ethyl alcohol.

In general, the same kind of experiments were carried out two or three times and the tabulated values are the averages of them.

Although it seems that Cs values for N/100 KCl aq. soln. disprove the simple additivity of the polarisation characters, most of them for N/10 KCl aq. solns. and especially for alcoholic solutions confirm our assumption with relatively high concordance. The Cs values of Cu-Pt system in Table II is something erratic, perhaps due to chemical instability of copper in aqueous solution, while the same system in alcoholic solution gives a good agreement between the observed value and the calculated one. The discrepancies which appear in "N/100 measurements" were

TABLE II

ADDITIVITY OF POLARISATION IMPEDANCES FOR AQUEOUS SOLUTIONS

System	$\Delta R(\Omega)$		$Cs(\mu F.)$	
	Obs.	Calc.	Obs.	Calc.
A) N/10 KCl aq. soln. at 28°C				
Pt-Pt	3.0	—	12.2	—
Ni-Ni	12.6	—	4.5	—
Cu-Cu	3.4	—	21.4	—
Ag-Ag	1.5	—	25.5	—
Ag-Pt	1.5	2.2	11.4	16
Cu-Pt	3.5	3.2	9.3	14
Ni-Pt	6.7	7.8	6.7	6.6
B) N/10 KCl aq. soln. at 0°C				
Ni-Ni	2.6	—	16.1	—
Ag-Ag	0.8	—	37.0	—
Ag-Ni	1.6	1.6	22.3	21.3
C) N/100 KCl aq. soln. at 0°C				
Ni-Ni	40	—	1.4	—
Ag-Ag	5	—	7.6	—
Pt-Pt	uncertain	—	1.6	—
Ag-Ni	10	20	6.8	2.4
Pt-Ni	uncertain	uncertain	4.7	1.5

TABLE III

ADDITIVITY OF POLARISATION IMPEDANCES FOR ALCOHOLIC SOLUTIONS

System	$\Delta R(\Omega)$		$Cs(\mu F.)$	
	Obs.	Calc.	Obs.	Calc.
Ni-Ni	70±30	—	4.8	—
Ag-Ag	130 „	—	12.5	—
Pt-Pt	uncertain	—	9.1	—
Cu-Cu	30±30	—	20.1	—
Ag-Ni	70±„	uncertain	6.5	6.9
Pt-Ni	140 „	„	6.1	6.0
Pt-Cu	50 „	„	12.6	12.5
Pt-Ag	140 „	„	11.1	10.4

not changed by the second runing reexamined one month after the first experiment.

It may be thought that in a dilute solution the solvent molecule as a role to make these discrepancies. In this connection, we made a series of experiments using a dilute alcoholic solution. The result confirmed the additive characters of the effect. This is seen in Table IV.

TABLE IV
ADDITIVITY FOR DILUTE ALCOHOLIC SOLUTIONS

System	Cs (μF.)	
	Obs.	Calc.
Ag-Ag	21.8	—
Ni-Ni	5.0	—
Ag-Ni	8.2	8.1

" N/100 values ", however, are only two sets of electrodes, therefore more detailed investigations with various sets of electrodes are necessary. At the same time the study must be carried out about more dilute solutions.

The polarisation resistance, ΔR,which is often called excess resistance, can be determined by changing the distance of electrodes; since the polarisation resistance is characteristic only of the electrode/solution interface and not affected by inter-electrode distance, if the frequency is kept constant.[1,6] Therefore we can obtain the ΔR value by plotting measured series resistance, Rs, against the electrode separation and read the extrapolated value of Rs at zero distance. Fig. 3a is one of the representative diagram for ΔR determinations. ΔR values for N/100 aqueous potassium chloride solutions and also for alcoholic solutions are very erratic, because our conductivity cell has no elaborate attachment to determine the interelectrode distance and therefore we can read only the order of the magnitude, when the solution is less conductive.

Summary

1) We attempted to prove that the polarisation characters, being measured as to a whole cell, can be attributed to each single electrode. This attempt was verified by most of the experiments.

2) The above success may be one of the experimental justifications to use a simple series circuit as the equivalent circuit of a conductivity cell.

3) Discordant results appearing in " N/100 measurements " are to be studied in more details.

The authors wish to express their great thanks to the effort made by Mr. Koichi Karaki, our former collaborator.

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Vat Dyes of Pyrazoloanthrone Series. V. Self Condensation of 5-Chloropyrazoloanthrone

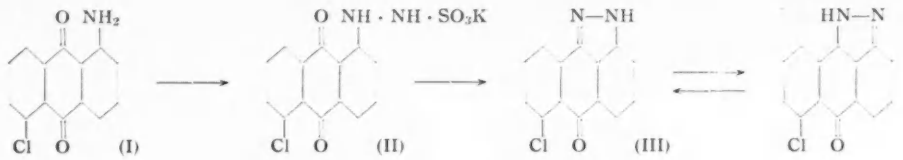
By Toshio MAKI and Hideo SEKI

(Received July 24, 1954)

Nuclear chloro derivatives of pyrazoloanthrone have been hitherto prepared from 1,x-dichloroanthraquinone and hydrazine hydrate in pyridine solution.[2] Recently Bradley and Geddes prepared 5-chloropyrazoloanthrone (III) also by this method from 1,5-dichloroanthraquinone,[3] but the obtained product had low and wide range of melting point (275–285°) and only after recrystallization melted at 298°. We have now synthesized 5-chloropyrazoloanthrone (III) from 1-amino-5-chloroanthraquinone (I) via potassium 5-chloroanthraquinonyl-1-hydrazine sulfonate (II) by application of the diazotization, followed by the

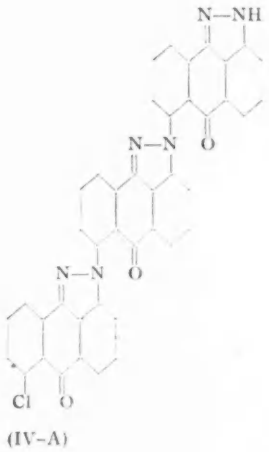
1) Read before the 6th Annual Meeting of the Chemical Society of Japan on April 5, 1953.

2) Ullmann, *Ber.*, **53**, 826 (1920).
3) *J. Chem. Soc.* **1952**, 1633.



treatment with sulfite and bisulfite and ring closure with conc. sulfuric acid analogous to our synthesis of pyrazoloanthrone from 1-aminoanthraquinone.[4] This method gives 5-chloro-pyrazoloanthrone of high purity in 79% yield of the theory. Even the crude product melted at 301–2° (corr.) and after recrystallization greenish yellow needles of m.p. 305–6° (corr.) were easily obtained.

Among the isomeric chloro derivatives of pyrazoloanthrone the 5-chloro compound is most reactive and we have found that it has an interesting behaviour of polymolecular self condensation, a new type of reaction hitherto never studied in the chemistry of anthraquinone derivatives. When 5-chloro-pyrazoloanthrone alone was heated in boiling nitrobenzene in the presence of sodium carbonate and copper for 25 hours the product was nearly 50%: 50% mixture of 3 molecular and 4 molecular self condensation product (IV-A and IV-B), which was ascertained by its properties



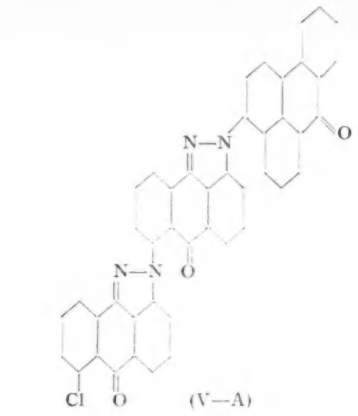
(IV-A)

(IV-B)

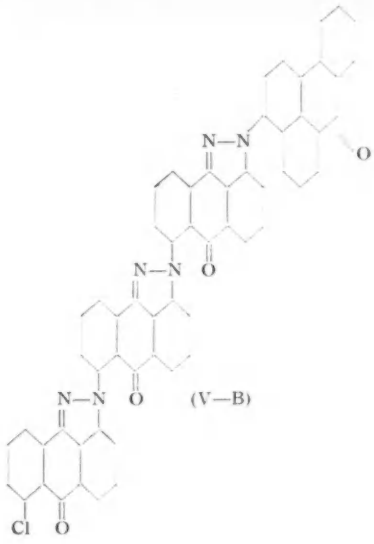
	5-Chloro-pyrazoloanthrone(III)	Self condensation product (IV-A and IV-B)
With aq. NaOH	Orange red solution	No color reaction
m.p.	305—6°	>400°
Cl% found	13.72	4.60
In *o*-dichlorobenzene	Soluble	Insoluble
Appearance	Greenish yellow needles	Yellow brown powder
In conc. H_2SO_4	Orange	Red orange
Precipitate with water	Yellow	Yellow brown

and estimation of the terminal chlorine atoms.

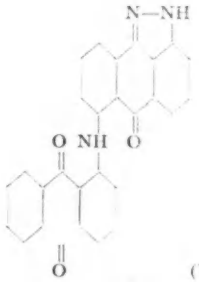
4) T. Maki, T. Akamatsu and M. Maezawa, *J. Chem. Soc. Japan. Ind. Chem. Section*, **54**, 245 (1951).



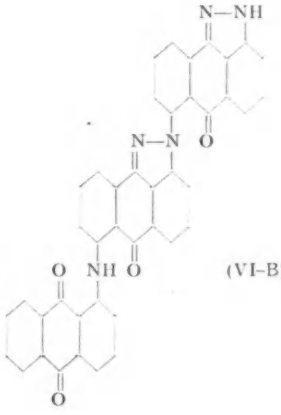
(V—A)



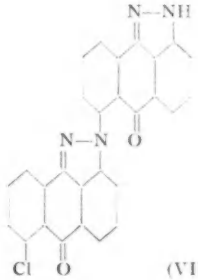
(V—B)



(VI-A)



(VI-B)



(VII)

In the presence of potassium carbonate, even without copper, the self condensation proceeded further and the obtained substance contains 3.80% Cl, which corresponds nearly to the 4 molecular condensation product (IV-B). This polymolecular self condensation occurs also in cases of other syntheses using 2 or more different components. Thus, when 5-chloro-pyrazoloanthrone and 3-bromobenzanthrone were boiled with nitrobenzene in the presence of sodium carbonate and copper for 15 hours the product was found to be a mixture of nearly 45% of (V-A) and 55% of (V-B), 1:2 and 1:3 product respectively, ascertained by the amount of recovered 3-bromobenzanthrone and estimation of Cl% and N% of the substance.

When 5-chloro-pyrazoloanthrone and 1-aminoanthraquinone were similarly boiled with naphthalene for 15 hours the chief product, insoluble in *o*-dichlorobenzene, was a mixture of nearly 34% of (VI-A) and 66% of (VI-B), 1:1 and 2:1 product respectively.

The part soluble in hot *o*-dichlorobezene, in this case, contained bimolecular self-condensation product (VII) and uncombined 1-aminoanthraquinone. The estimation of the amounts of these soluble components was useful for the determination of the proportion of (VI-A) and (VI-B).

Experimental Part

5-Chloro-pyrazoloanthrone (III). — 1-Amino-

5-chloroanthraquinone (I)[5] (12.88g., 1 mol. ratio) was dissolved in 64.4g. of conc. sulfuric acid (97.0%) and sodium nitrite (3.65g., 1.06 mol. ratio), dissolved in 36.5g. of ice cold conc. sulfuric acid, was added at 2° and agitated for 30 minutes at 5°. The diazo solution was poured on 150g. of ice and after the addition of 14.6g. of anhydrous sodium sulfate stirring was continued for 30 minutes keeping the temperature below 10°. The precipitated diazo compound was filtered, agitated with 250g. of ice water and sodium bicarbonately was carefully added until the litmus-neutral point was obtained. The presence of 2 drops of lauryl alcohol is convenient as an antifoaming agent. To the neutralized diazo compound 59.0g. of 16% sodium sulfite (1.5 mol. ratio), freshly prepared from sodium hydroxide and sulfur dioxide, was added, kept 1 hour at 10°, then 1 hour at 30° and to this diazo sulfonate 21.6g. of freshly prepared 36% sodium bisulfite (1.5 mol. ratio), together with 2 cc. of conc. hydrochloric acid and 2 cc. of water, was given, warmed up to 90° and agitated at this temperature for 1 hour. The hot solution was filtered in order to remove a small amount of dark brown insoluble by-product (2.9% of the starting material) and 45g. of potassium chloride was added to the orange red filtrate and allowed to stand over night. The red crystalline precipitate of potassium 5-chloroanthraquinonyl- 1-hydrazine sulfonate (II) was collected and dried in vacuum. The yield was 21.9g. This was then dissolved in 175g. of conc. sulfuric acid (99.6%) and kept at 100° for 3 hours on a boiling water bath. 5-Chloro- pyrazoloanthrone was obtained by pouring the acid solution into water. The yield of the crude product, m.p. 301–2° (corr.), was 10.05g. or 79.0% of the theory. After recrystallization from *o*-dichlorobenzene greenish yellow needles of highest purity, m.p. 305–6° (corr.), were obtained. Its conc. sulfuric acid solution is orange, and a yellow precipitate is formed by the addition of water. Like the unsubstituted pyrazoloanthrone its iminohydrogen is so sensitive to alkali that it dissolves in dilute sodium hydroxide with intense orange red color, which is very useful for its detection even in cases of minute quantities. As shown in our previous report[6] the tautomerism must, of course, exist also in 5-chloro-pyrazoloanthrone. Found: N, 10.74; Cl 13.72; Calcd. for $C_{14}H_7ON_2Cl$ (III): N, 11.01%; Cl 13.92%.

Self Condensation of 5-Chloro-pyrazoloanthrone.—A mixture of 1.268g. (1 mol. ratio) of 5-chloro-pyrazoloanthrone (III), 0.530g. (1 mol. ratio) of anhydrous sodium carbonate and 0.063g. (0.2 atomic ratio) of precipitated metallic copper was kept boiling with 25.4g. of nitrobenzene under reflux and stirring for 25 hours. Nitrobenzene was then removed by steam distillation and the precipitate, after collecting and drying, was dissolved in 30 times to quantity of conc. sulfuric acid and filtered through asbestos in order to remove the insoluble copper. By pouring the conc. sulfuric acid filtrate into water the condensation product was obtained, which was washed neutral and dried at 110°. The yield was 1.10g. or 86.5% of the starting material. It is a yellow brown powder of m.p. higher than 400°, with no color reaction sodium hydroxide and perfectly free from 5-chloro-pyrazoloanthrone. It is insoluble in organic solvents, soluble in conc. sulfuric acid with red orange color, and a yellow brown precipitate is formed from the acid solution by water. Found: Cl, 4.60; calcd. for $C_{42}H_{19}O_3N_5Cl$ (IV-A): Cl, 5.14%; calcd. for $C_{57}H_{25}O_4N_8Cl$ (IV-B): Cl, 3.91%. The substance corresponds neary to 50%: 50% mixture of (IV-A) and (IV-B). Contrary to 2,2'-dipyrazoloanthronyls this substance is insoluble in alkaline hydrosulfite as its constituents have no conjugation between the two carbonyls.

Condensation of 5-Chloro-pyrazoloanthrone with 3-Bromobenzanthrone.[7] — 5-Chloro-pyrazoloanthrone (2.117g., 1 mol. ratio) and anhydrous sodium carbonate (0.974g., 1.1 mol. ratio) were boiled with 31.8g. of nitrobenzene for 1 hour. The heating was interrupted for a short time, 2.834g. (1.1 mol. ratio) of 3-bromobenzanthrone together with 0.106g. (0.2 atomic ratio) of precipitated metallic copper being added, and the whole was further boiled for 15 hours. After distilling off the solvent by steam and removing the insoluble copper with conc. sulfuric acid as in the above experiment, 4.64g. of crude condensation product was obtained. As the crude product is perfectly indifferent to sodium hydroxide and gives no red color it was confirmed that it contains no more 5-chloro-pyrazoloanthrone. It was then boiled with 46.4g. of *o*-dichlorobenzene for 1 hour and filtered, when the purified condensation product, 2.32g. or 50.0% of the crude product, was obtained as the insoluble and 1.94g. (0.75 mol. ratio) of unchanged 3-bromobenzanthrone recovered from the filtrate by steam distillation. So it became known that approximately 0.35–0.4 mol. of 3-bromobenzanthrone had actually condensed with 1 mol. of 5-chloro-pyrazoloanthrone. The purified condensation product is a brown yellow powder of m.p. higher than 400°, insoluble in organic solvents and soluble in conc. sulfuric acid with orange color. Found: N,8.67; Cl, 4.28; calcd. for $C_{45}H_{21}O_3N_4Cl$ (V-A): N, 8.00%; Cl, 5.07%; calcd. for $C_{59}H_{27}O_4N_5Cl$ (V-B): N, 9.15%; Cl, 3.56%. The substance corresponds nearly to a mixture of 45% of (V-A) and 55% of (V-B).

Condensation of 5-Chloro-pyrazoloanthrone with 1-Aminoanthraquinone.[7] —A mixture of 1.015g. (1 mol. ratio) of 5-chloro-pyrazoloanthrone, 0.893g. (1 mol. ratio) of 1-aminoanthraquinone, 0.424g. (1 mol.ratio) of anhydrous sodium carbonate and 0.051g. (0.2 atomic ratio) of precipitated copper was kept boiling with 20g. of naphthalene

5) Obtained by the sodium sulfide reduction of 1-chloro-5-nitroanthraquinone in 91.8% yield and after recrystallization from o-dichlorobenzene melted at 219° (corr.). 1-Chloro-5-nitroanthraquinone was prepared from potassium 5-nitroanthraquinone-1-sulfonate by the chlorate method in 94% yield and a sample of m.p. 316° (corr.) was obtained after recrystallization from *o*-dichlorobenzene. See also T. Maki and Y. Nagai, *J. Chem. Soc. Ind. Japan*, **33**, 464B (1930).

6) T. Maki and T. Akamatsu, *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 281, 326 (1951).

7) Compare with *G. P.* 520395, *Frdl.* **17**, 1291

under reflux and stirring for 15 hours. As in the above experiments the crude condensation product was obtained after the steam distillation of naphthalene and after removing the copper by the treatment with conc. sulfuric acid. The yield was 1.61g. The crude product is perfectly free from the starting 5-chloro-pyrazoloanthrone as it shows no red color reaction with sodium hydroxide. A small quantity of chlorine (1.5%Cl) found in the crude substance indicates the presence of about 20% of bimolecular self-condensation product (VII) (calcd. Cl 7.50%), because it can be removed by dissolving in boiling *o*-dichlorobenzene. When the crude product (1.61g.) was boiled with 48.3g. of *o*-dichlorobenzene, hot filtered 0.70g. (44% of the crude product) of chlorine free condensation product was obtained as the insoluble. From the filtrate 0.50g. of unchanged 1-aminoanthraquinone and 0.32g. of the chlorine compound (VII), corresponding to 0.34g. of 5-chloro-pyrazoloanthrone, were recovered. So it was found that about 0.39g. (0.44 mol. ratio) of 1-aminoanthraquinone had actually condensed with 0.67 g. (0.66 mol. ratio) of 5-chloro-pyrazoloanthrone. The purified, chlorine free condensation product is a red brown powder of m.p. higher than 400°, hardly soluble in organic solvents, indifferent against alkali, but soluble in conc. sulfuric acid brown, and brown red precipitate is produced from the acid solution by the addition of water. From these data it is concluded that the substance, insoluble in hot *o*-dichlorobenzene, is a mixture of nearly 34% of 1 : 1 condensation product (VI-A) and 66% of 2 : 1 condensation product (VI-B). Found: N,10.35; calcd. for $C_{28}H_{15}O_3N_3$ (VI-A): N, 9.52%; calcd. for $C_{42}H_{21}O_4N_5$ (VI-B): N, 10.62%.

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Antituberculous Compounds. IV. Thiosemicarbazones and Related Compounds

By Tamio NISHIMURA

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α-Bromo-4-nitrocinnamaldehyde thiosemicarbazone has been found to posses *in vitro* action against *Staphylococcus aureus* and *Escherichia coli*.[1] In the present study, semicarbazones and guanylhydrazones of α-bromo-4-nitrocinnamaldehyde (I) and 1-(4-nitrophenyl)-2-bromo-1-buten-3-one were prepared in an attempt to increase the biological effect. Corresponding derivatives of 4-nitrocinnamaldehyde (II) and 4-nitrobenzalacetone were prepared in order to examine the effect of Br-substitution at the α-position of α,β-unsaturated carbonyl compounds. Nitromethane derivatives of I and II were also synthesized.

Furthermore, thiosemicarbazones of 4-nitro, 4-amino, and 4-acetamido-acetophenones were prepared in an attempt to compare their antituberculous activities with those of their vinylogs synthesized previously.[2]

Experimental[3]

α-Bromo-4-nitrocinnamaldehyde.—To a solution of 8.9 g. of 4-nitrocinnamaldehyde[4] in 80 cc. of glacial acetic acid was added 8 g. of bromine. When the red color of the mixture had almost completely disappeared, 6.9 g. of anhydrous potassium carbonate was added. After the evolution of gas had ceased, the mixture was heated in a water bath for ten minutes, giving 11.5 g. of slightly yellow crystals melting at 137–138°. On adding water the filtrate produced a further crop melting at 133–134° which yielded 0.4 g. of the product melting at 136–138° on recrystallization from 10 cc. of ethanol. Both crops were recrystallized from ethanol to give 11 g. (86%) of the desired product melting at 138–139°.[5]

Thiosemicarbazone.—To a suspension of 0.8 g. of α-bromo-4-nitrocinnamaldehyde in 20 cc. of hot ethanol was added 0.3 g. of thiosemicarbazide and the whole stirred in a water bath for ten minutes to give yellow precipitates, yield 1 g. (90%), m.p. 218° (decompn.) Recrystallization from ethanol gave slightly yellow long needles, m.p. about 214° (decompn.). Found: N, 16.88%. Calcd. for $C_{10}H_9N_4O_2SBr$: N, 17.00%.

Semicarbazone.—The crude product obtained by heating a mixture of the aldehyde, semicarbazide, and ethanol was recrystallized three times from ethanol, giving tiny yellow prisms melting at 223° (decompn.) in 32% yield. Found: N, 17.91%. Calcd. for $C_{10}H_9N_4O_2Br$: N, 17.90%).

Guanylhydrazone hydrochloride.—A mixture of 1.3 g. of the aldehyde, 0.7 g. of aminoguanidine bicarbonate[6], and 10 cc. of ethanol was acidified

1) Katsuhiko Tago and Tamio Nishimura, Presented before the Kanto regional meeting of Nippon Saikin Gakkai, June 27, 1953; chemotherapy **2**, 157—161 (1954).
2) Tamio Nishimura, This Bulletin, **26**, 253 (1953).
3) All temperatures are uncorrected.
4) Tamio Nishimura, This Bulletin, **25**, 54 (1952).
5) Reported m.p. 136°; Zincke v. Hagen, *Ber.*, **17**, 1816 (1884). Einhorn and Gehrenbeck, *Ann.*, **253**, 351 (1889).
6) R. L. Shriner and Fred W. Neumann, "Organic Syntheses" Vol. 26, p. 7.

with concentrated hydrochloric acid[7] and heated in a water bath for several minutes. Pale yellow long prisms were obtained from ethanol and conc. hydrochloric acid; m.p. 265° (decompn.), yield 1.4 g. (80%). Found: Cl, 10.35%. Calcd. for $C_{10}H_{11}N_5O_2BrCl$: Cl, 10.17%.

4-Nitrocinnamaldehyde.—This compound was prepared as reported before.[4]

Semicabazone.—A solution of 0.9 g. of the aldehyde, and 0.6 g of acetone semicarbazone in 50 cc. of ethanol was adjusted to pH 3.0 with 10% hydrochloric acid and heated in a water bath for thirty minutes. Crystals were filtered, washed well with ethanol, suspended in 20 cc. of hot ethanol, filtered hot, and washed again with ethanol to give 1 g. (84%) of the desired product, m.p. 232° (decompn.), yellow plates. Found: N, 23.82%. Calcd. for $C_{10}H_{10}N_4O_3$: N, 23.95%).

Guanylhydrazone hydrochloride.—Tiny yellow prisms (from ethanol and concentrated hydrochloric acid), easily soluble in hot ethanol and hot water and insoluble in hot benzene, yield 64%, m.p. 238° (decompn.). Found: Cl, 13.50%. Calcd. for $C_{10}H_{12}N_5O_2Cl$: Cl, 13.15%.

4-Nitrobenzalacetone.—This compound was synthesized as reported previously.[2]

Semicarbazone.—From 0.96 g. of the ketone and semicarbazide in ethanol was obtained 1.1 g. (89%) of the desired product, m.p. 234° (decompn.), canary yellow crystals. The crude material (0.2 g.) dissolved in 25 cc. of hot pyridine gave tiny needles melting at 235° (decompn.) on adding 40 cc. of water. Found: N, 22.21%. Calcd. for $C_{11}H_{12}N_4O_3$: N, 22.57%.

Guanylhydrazone hydrochloride.—Tiny yellow needles melting at 270° (decompn.) obtained from 0.96 g. of the ketone were recrystallized form 150 cc. of ethanol containing a small amount of concentrated hydrochloric acid, giving 1.2 g. (85%) of the pure hydrochloride melting at 270° (decompn.). Found: Cl, 12.59%. Calcd. for $C_{11}H_{14}N_5O_2Cl$: Cl, 12.50%.

1-(4-Nitrophenly)-2-bromo-1-buten-3-one. — This compound was prepared according to the method reported before.[2]

Semicarbazone.—Long pale yellow prisms (from ethanol) melting at 229° (decompn.) from the ketone and semicarbazide, yield 82%, halogen test positive, Found: N, 17.10%. Calcd. for $C_{11}H_{11}N_4O_3Br$: N, 17.13%.

Guanylhydrazone hydrochloride.—Yellow prisms (from ethanol and concentrated hydrochloric acid), m.p. 249–250° (decompn.), yield 87%. Found: Cl, 9.74%. Calcd. for $C_{11}H_{12}N_5O_2BrCl$: Cl, 9.78%.

ω-Nitro-4-nitrostyrene.—The same procedure as mentioned by David E. Worral[8] in their description of the synthesis of nitrostyrene, was used to prepare this compound.

From 1.5 g. of 4-nitrobenzaldehyde and 0.6 cc. of nitromethane[9] was obtained 0.5 g. (26%) of the desired product melting at 203–204° (decompn.)[10], consisting of yellow prisms (from ethanol).

1-(4-Nitrophenyl)-4-nitro-1,3-butadiene. — The crude material obtained similarly as above from 1.8 g. of 4-nitrocinnamaldehyde and 0.7 g. of nitromethane was recrystallized from ethanol, giving 0.4 g. (18%) of yellow needles, m.p. 200–201° (decompn.). Found: N, 12.69%. Calcd. for $C_{10}H_8N_2O_4$: N, 12.73%.

1-(4-Nitrophenyl)-2-bromo-4-nitro-1,-3butadiene.—α-Bromo-4-nitrocinnamaldehyde (1.3g.) and nitromethane (0.4 cc.) were condensed at 5–12°. On recrystallization from ethanol of the crude product, 0.32 g. (15%) of tiny yellow prisms, m.p. 182–182.5°, were obtained. Found: N, 9.49%. Calcd. for $C_{10}H_7N_2O_4Br$: N, 9.37%.

4-Acetamidoacetophenone.—A suspension of 2.7 g. of 4-aminoacetophenone in 27 cc. of water was treated with 2.7 cc. of acetic anhydride to give 3 g. (85%) of the desired product, consisting of colorless prisms, m.p. 169–170°.[11]

4-Nitroacetophenone.—The procedure described by Sugasawa[12] was used with some modification.

4-Aminoacetophenone (6.75 g.) was dissolved in 65 cc. of water and 8 cc. of nitric acid (sp. gr. 1.42) and diazotized with a solution of 9.6 g. of sodium nitrite in 20 cc. of water. The diazo solution was run slowly into a mixture of water (55 cc.), cuprocupric sulfite (prepared from cupric sulfate (12.5 g.) in water (50 cc.) and sodium hydroxide (4 g.) in water (20 cc.)), and sodium nitrite (13.8 g.). After stirring for two hours at room temperature the reaction mixture was extracted six times with 50 cc. portions of ether, the ether removed, and the residue recrystallized from methanol to give 5.07 g. (63%) of the desired product, m.p. 80–81°. A recrystallized sample showed m.p. 82–82.5°.

4-Aminoacetophenone thiosemicarbazone. — A mixture of 0.68 g. of 4-aminoacetophenone, 0.46 g. of thiosemicarbazide and 25 cc. of water was heated in a water bath for nine houres, but the reaction did not take place. Then the mixture was adjusted to pH 3.2[14] with glacial acetic acid and heated for thirty minutes to give 0.84 g. (81%) of the desired product, slightly yellow plates, m.p. 182–183° (decompn.). Recrystallization from ethanol gave a sample melting at 185° (decompn.). Found: N, 26.55%. Calcd. for $C_9H_{12}N_4S$: N, 26.90%.

4-Acetamidoacetophenone thiosemicarbazone.—A solution of 0.46 g. of thiosemicarbazide in 10 cc. of water was added to a solution of 0.89 g. of 4-acetamidoacetophenone in 10 cc. of ethanol.

7) J. Thiele and R. Bihan. *Ann.*, **302**, 311 (1898).
8) David E. Worrall, "Organic Syntheses" Col. Vol. I. p. 495.
9) F. C. Whitmore and Marion G. Whitmore, Ibid., Col. Vol. I. p. 393.
10) Reported mp. 196—199°. See Johannes Thiele, *Ber.*, 1294 (1899).
11) Klingel (*Ber.*, **18**, 2691 (1885)) and Kunckell (*Ber.* 33, 2641 (1900) reported m.p. 166—167°.
12) S. Sugasawa, N. Sugimoto, J. Iwao and Y. Nakamura, *J. Pharm. Soc. Japan.*, **71**, 225 (1951).
13) H. H. Hodgson, A. P. Mahadevan, and E. R. Ward, "Organic Syntheses" Vol. 23, p. 52.
14) A maximum value of condensation velocity of furfural and semicarbazide was found to be at pH 3.13 by J. B. connant and P. D. Bartlett, *J. Am. Chem. Soc.*, **54**, 2881 (1932).

The whole was adjusted to pH 3.2 with glacial acetic acid, heated in a water bath for one hour, and cooled to yield 1.14 g. (91%) of the desired product, slightly yellow plates, m.p. 223.5° (decompn.) (from ethanol). Found: N, 22.27%. Calcd. for $C_{11}H_{14}N_4OS$: N, 22.39%.

4-Nitroacetophenone thiosemicarbazone. — Similarly was obtained the desired product, yellow needles melting at 240° (decompn.), yield 82%, Found: N, 23.38%. Calcd. for $C_9H_{10}N_4O_2S$: N, 23.38%.

Summary

1) Semicarbazones and guanylhydrazones of 4-nitrocinnamaldehyde, 4-nitrobenzalacetone, α-bromo-4-nitrocinnamaldehyde, and 1-(4-nitrophenyl)-2-bromo-1-buten-3-one, nitromethane derivatives of 4-nitrobenzaldehyde, 4-nitrocinnamaldehyde, and α-bromo-4-nitrocinnamaldehyde, and thiosemicarbazones of 4-amino, 4-acetamido-, and 4-nitroacetophenones were prepared for evaluation of their antibacterial activity.

2) Condensation of the acetophenones with thiosemicarbazide was found to proceed smoothly at pH 3.2 but not at pH 7.

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Enzymatic Microdetermination of Nitrate

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As the color reactions for nitrate so far known are less sensitive and less specific than the Griess-Ilosvay reaction for nitrite, nitrate has often been estimated as nitrite after reduction. However, ordinary reducing agents are not sufficiently specific and it is generally difficult to reduce nitrate quantitatively to nitrite.

We tried, therefore, to reduce nitrate to nitrite quantitatively by a specific enzyme—nitrate reductase,* and to determine nitrate indirectly by the Griess-Ilosvay reaction for nitrite.

Concerning nitrate reductase, R. Sato and one of us (Egami)[1] have shown that a cell-free extract obtained by the ultrasonic destruction of certain strains of *Escherichia coli* contains nitrate reductase, but not nitrite reductase, and nitrate can be reduced to nitrite by the enzyme preparation in the presence of an appropriate hydrogen donor such as formic acid and an intermediary hydrogen carrier such as methylene blue.

Analytical Procedure

Enzyme Preparation.—A strain of *E. coli* (given by Dr. S. Yamagutchi) is cultured at first on the KNO_3(0.1%), peptone (1%), bouillon (1%), agar plate for 15—17 hours at pH 7.4, 37°C. The preparatory culture is inoculated on the peptone bouillon agar plate without nitrate and incubated for 15—17 hours at 37°C. The bacterial cells harvested from 2—3 litre plate culture are washed several times by centrifugation until the supernatant is free from nitrite. The bacterial cells are suspended in 50—60 ml. of distilled water and destroyed by ultrasonic irradiation (490 K.C. for 30—40 min.). Then the bacterial debris are centrifuged off (7000×g. for 30—40 min.) at 0°C. To the cooled supernatant, is added an equal volume of saturated ammonium sulfate solution (adjusted to pH 7.0) under stirring. The formed precipitate containing nitrate reductase and formic dehydrogenase is centrifuged (7000×g. for 30 min.) at 0°C and dissolved in 20—30 ml. of cold water. The enzyme solution is dialysed against running water for 24 hours. Then the enzyme solution is freeze-dried, and 700—800 mg. of the dried preparation is obtained. The dried preparation in evacuated ampoule maintains its activity for at least 3 months in an ice-box.

Solutions required. — a. Enzyme solution: The freeze-dried powder is dissolved in distilled water (2mg./1 ml.).

b. Methylene blue or FAD**(1/200 M), sodium formate (1/5 M), phosphate buffer (1/5 M) (pH

* In this connection, it should be added that R. Williams et al. have used living cells of *E. coil* as reducing catalyst. Their method is for clinical use and less accurate (*J. Lab. Clin. Med. St Louis*, **41**, 157, (1953)).

1) F. Egami and R. Sato, *J. Chem. Soc. Japan*, **68** 39, (1947); **69** 160 (1948); *Proc. Japan Acad.*, **24** 29 (1948).

* Flavin adenine dinucleotide.

* If FAD is used in place of methylene blue, the process of decoloration may be omitted.

7.2) mixed solution.

c. Saturated aqueous solution of uranyl acetate.

d. Griess-Ilosvay reagent:

Solution 1. Sulfanilic acid (10.5 g.), sodium acetate (6.8 g.) and glacial acetic acid (300 ml.) are dissolved in 600 ml. of distilled water. The soluion is boiled for 3 min. and diluted to 1 l.

Solution 2. α-Naphthylamine (5.0 g.) is added to 1 l. of boiling water, then 5 ml. of conc. hydrochloric acid is added to the solution.

Before use, equal volumes of the two solutions are mixed together.

Method of analysis—1. Place 1 ml. of solution a, 0.5 ml. of solution b and 2 ml. of test solution into a Thunberg tube.

2. Evacuate the tube by aspiration.
3. The tube is allowed to stand at 37°C for 1.5—2.0 hours. Here the reduction takes place.
4. To 2 ml. of solution c in a centrifugal tube, are added 3 ml. of the reaction mixture and a small amount of kaolin powder for decoloration.
5. After centrifugation, to 4 ml. of the clear supernatant is added 1 ml. of Griess-Ilosvay reagent.
6. Then, it is colorimetrically estimated as usual.

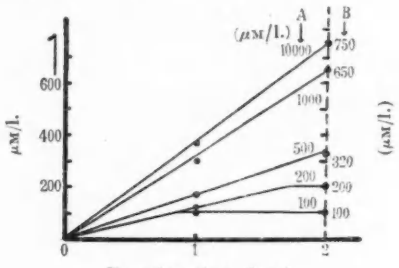
The authors measured the extinction at 530 mμ with Coleman's spectrophotometer. As blank test solution, the similarly treated solution with 2 ml. of distilled water in place of the test solution should be used.

Remarks.—(1) When nitrite coexists with nitrate, nitrite should be estimated at first as usual, and the value should be subtracted from the total value obtained after reduction.

(2) When the test solution is too concentrated (>100μM/l. nitrate), it must be diluted preliminarily, otherwise the complete reduction can not be attained in 2 hours, as is shown in Fig. 1. So before the accurate analysis, the approximate nitrate concentration must be estimated by measuring the nitrite produced in 2 hours. The test solution is then diluted to an appropriate concentration (10—100μM/l.), and the accurate analysis should be carried out.

Some Examples of Analyses

Some Examples of Analyses with Nitrate and Nitrite Solutions of the Known Concentration.—Some of the experimental results are summarized in Table I, II and III. As shown in Table I and II respectively, nitrate (10—100μM/l.) can be quantitatively estimated by this method and nitrite (50,100μM/l) be quantitatively recovered. Table III shows that the mixture of nitrate and nitrite is quite satisfactorily estimated as the total sum, so nitrate can be determined by subtracting the quantity of nitrite estimated directly as usual.



A: Nitrate concentration in test solution used in enzymatic reduction.

B: Nitrite concentration produced after 2 hours enzymatic reduction.

Fig. 1. Experimental scale for approximate estimation of nitrate concentration.

TABLE I

DETERMINATION OF NITRATE IN STANDARD SOLUTION

Nitrate concn. present (μM/l.)	Nitrite concn. determd. (μM/l.)	Nitrate recovery (%)
10	9.5, 10.5	95, 105
25	25.0, 26.0, 26.5	100, 104, 106
50	48.5, 48.0	97, 96
100	102.0, 99.0, 97.0	102, 99, 97

TABLE II

RECOVERY TESTS OF NITRITE IN NITRATE DETERMINATION

Nitrite concn. present (μM/l.)	Nitrite concn. determd. (μM/l.)	Nitrite recovery (%
50	52.0, 52.0	104, 104
100	98.0	98

TABLE III

DETERMINATION OF NITRATE IN MIXED SOLUTIONS OF NITRATE AND NITRITE

(1) Nitrate concn. present (μM/l.)	(2) Nitrite concn. present (μM/l.)	(3) Nitrite concn. preliminarily determd. (μM/l.)	(4) Nitrate plus nitrite concn. determd. (μM/l.)	(5) Nitrate concn. determd. :(4)—(3) (μM/l.)	(6) Nitrate recovery. (%)
17.0	19.5	19.5	35.0	15.5	91
20.0	6.0	6.0	26.0	20.0	100
20.0	20.0	20.0	38.0	18.0	90
20.0	40.0	40.0	61.0	21.0	105
100.0	40.0	40.0	144.0	104.0	104

Some Examples of Practical Applications.—The method was applied to the estimation of nitrate in human urine, horse serum, spinach leaf extract, sea water and rain water. As a small quantity of nitrate added to these natural test solutions were always quantitatively recovered as shown in Tables IV—VIII, it may be concluded that the method is satisfactory for the estimation of nitrate in these natural samples.

TABLE IV

DETERMINATION OF NITRATE IN HUMAN URINE

Human urine freshly obtained is diluted according to Remarks (2), then used as a sample for accurate analysis. The sample contains no nitrite.

Sample 1. (400 fold diluted)

	Nitrate concn. determd. (μM/l.)	(Mean) (μM/l.)		
Sample alone	15.0		Nitrate concn. in original human urine	
	15.0	15.0	15.0μM/l. $\times$ 400 = 6.0 $\times$ 10^{-3}M/l. = 84 mg. nitrate-N/l.	
Sample + 25μM/l. nitrate.	38.5		Recovery of 25μM/l. nitrate added (μM/l.)	Recovery (%)
	38.0	38.5	23.5	94

Sample 2. (100 fold diluted)

	Nitrate concn. determd. (μM/l.)	(Mean) (μM/l.)		
Sample alone	63.0		Nitrate concn. in original human urine	
	61.5		63.0μM/l. $\times$ 100 = 6.3 $\times$ 10^{-3}M/l. = 88 mg. nitrate-N/l.	
	65.0	63.0		
Sample + 25μM/l. nitrate	87.0		Recovery of 25μM/l. nitrate added (μM/l.)	Recovery (%)
	86.0	86.5	23.5	94

TABLE V

DETERMINATION OF NITRATE IN HORSE SERUM

To the freshly prepared horse serum, is added sodium fluoride (final concn. 1%) as an antiseptic.
This sample contains no nitrite.

	Nitrate concn. determd. (μM/l.)	(Mean) (μM/l.)		
Sample alone	35.0, 34.0		Nitrate concn. in horse serum	
	32.0, 33.0		34μM/l. = 0.5 mg. nitrate-N/l.	
	34.0, 35.0	34.0		
Sample + 25μM/l. nitrate	57.0		Recovery of 25μM/l. nitrate added. (μM/l.)	Recovery (%)
	57.0	57.0	23.0	92
Sample + 50μM/l. nitrate	82.0		Recovery of 50μM/l. nitrate added.	Recovery
	80.0		(μM/l.)	(%)
	80.0	81.0	47.0	94

TABLE VI

DETERMINATION OF NITRATE IN SPINACH LEAF EXTRACT

Minced young spinach leaves are immersed in boiling water, then homogenized and centrifuged (10000×g. for 30 min.). The green supernatant obtained—the dry weight of 1 ml. of this original extract amounts 3.2 mg.—is diluted 200 fold according to Remarks (2), then used as an sample for accurate analysis. This sample contains no nitrite.

	Nitrate concn. determd. (μM/l.)	(Mean) (μM/l.)	
Sample alone	36.0		Nitrate concn. in original spinach leaf extract
	36.0	36.0	$36\mu M/l. \times 200 = 7.2 \times 10^{-3} M/l. = 0.1$ mg. nitrate-N/ml. $= 0.03$ mg. nitrate-N/mg. dry weight
Sample + 25μM/l. nitrate	60.0		Recovery of 25μM/l. nitrate added (μM/l.)
	59.0		
	59.0	59.0	23.0
Sample + 50μM/l. nitrate	86.0		Recovery of 50μM/l. nitrate added (μM/l.)
	84.0	85.0	49.0

Recovery (%)
92
Recovery (%)
98

TABLE VII

DETERMINATION OF NIRATE IN SEA WATER

Prior to the determination of nitrate, the nitrite concn. of the sea water is determined according to Remarks (1). In this case, it is necessary to lower the high salt concn. of the sea water, by which nitrate reductase activity is inhibited. So the ordinary analytical method is slightly modified by adding excess 1 ml. of distilled water at Step. 1 and converting the total volume of reaction mixture to 4.5 ml.

	Nitrite concn preliminarily determd. (μM/l.)	Nitrate plus nitrite concn. determd. (μM/l.)	Nitrate concn. determd. (μM/l.)	(Mean.) (μM/l.)	
Sample alone	2.0	15.0	13.0		Nitrate concn. in sea water
	2.0	17.0	15.0	14.0	$14\mu M/l. = 0.20$ mg. nitrate-N/l.
Sample + 25μM/l. nitrate	2.0	40.5	38.5		Recovery of 25μM/l. nitrate added (μM/l.)
	2.0	39.5	37.5	38.0	24.0

Recovery (%)
Recovery (%)
96

TABLE VIII

DETERMINATION OF NITRATE IN RAIN WATER

Prior to the determination of nitrate, the nitrite concn. of the rain water is determined according to Remarks (1). In this case, the nitrate concn. of the test sample is very dilute. So, the ordinary analytical method is slightly modified by using 3 ml. of the test sample and dissolving the enzyme powder in 3.5 ml. reaction mixture.

	Nitrite concn. preliminarily determd. (μM/l.)	Nitrite plus nitrite concn. determd. (μM/l.)	Nitrate concn. determd. (μM/l.)	(Mean) (μM/l.)	
Sample alone	0.5	6.5	6.0		Nitrate concn. in rain water
	0.5	6.0	5.5	6.0	$6.0\mu M/l. = 0.08$ mg. nitrate-N/l.
Sample + 12.5μM/l. nitrate	0.5	18.5	18.0		Recovery of 12.5μM/l. nitrate added. (μM/l.)
	0.5	18.5	18.0	18.0	12.0

Recovery (%)
Recovery (%)
96

Summary

1) On the principle of the colorimetry of nitrite produced by enzymatic reduction, a method of microdetermination of nitrate was established.

2) This method can be applied to 10—100μM/l. nitrate solution. 2 ml. of the solution (1.2—12 μg. NO^-_3 or 0.28—2.8 μg. nitrate-N) is sufficient for an analysis.

3) This method is successfully applied to the estimation of nitrate in human urine, horse serum, spinach leaf extract, sea water and rain water.

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Department of Chemistry, Faculty of Science, Nagoya University

Diphenylcarbazone as an Internal Indicator in Volumetric Analysis. Part I. Determination of Ferrocyanide by Lead Nitrate

By G. S. DESHMUKH

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The standard methods of ferrocyanide determination may be classified broadly as follows: (a) those leading to its quantitative oxidation under certain operative conditions by such oxidants like Ce^{IV}, KIO_3 and $KMnO_4$[1-3]; (b) those involving the formation of stable complexes of known composition, especially the titration of zinc salt solutions against $K_4Fe(CN)_6$[4] and (c) titrations with $AgNO_3$[5] or $Pb(NO_3)_2$[6] using fluorescein or sodium alizarin sulfonate as adsorption indicators. According to Müller and Gäbler, potentiometric titration of standard lead nitrate against $K_4Fe(CN)_6$ gives reproducible and accurate results.[7]

It is known that in the well known microtest for Hg^{++} by diphenylcarbazone, Pb^{++} interferes due to its reaction with the reagent to develop an intense red or pink color. An aqueous solution of $K_4Fe(CN)_6$ does not, however, produce any characteristic color on the addition of diphenylcarbazone other than the brown or orange color of its alcoholic solution. This, as also the fact that besides Alizarine S no other indicator has been successfully adopted for the titrimetric detemination of ferrocyanide by $Pb(NO_3)_2$, suggested the investigation of this volumetric procedure using diphenylcarbazone as an internal indicator.

Experimental

Standard solutions of lead nitrate were prepared by dissolving accurately weighed quantities of a Merck's guaranteed reagent grade sample in appropriate volume of water; the lead content was checked by the chromate method. Laboratory reagent grade $K_4Fe(CN)_6$ was used for preparing solutions of various concentrations. The quantity of ferrocyanide in an aliquot portion of the solution was determined by standard ceric sulfate with ferroin as the indicator and potentiometrically. To 10 ml. of $K_4Fe(CN)_6$ about 1 ml. of the saturated alcoholic solution of diphenylcarbazone was added and the brown or orange colored solution was titrated slowly with constant stirring against standard lead nitrate. With the formation of lead ferrocyanide, the color faded gradually to pale yellow or brown and the end point was marked with a sharp change to purple. This is easy to detect and does not involve the risk of over-titration. It is, however, possible to rectify the error due to surpassing of the end point by running in a measured quantity of ferrocyanide and continuing the titration as usual. A reverse titration indicating a color change from purple to pale yellow or almost colorless though possible, was found to be less sharp and accurate. The molecular ratio of Pb: $K_4Fe(CN)_6$, calculated from the quantity of $Pb(NO_3)_2$ reacting with ferrocyanide at the equivalent point, showed that the composition of the precipitate corresponds to $Pb_2Fe(CN)_6$ or 2Pb—1$K_4Fe(CN)_6$. These results are shown in the Table.

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6) R. Burstein, *Z. anorg. allgem. Chem.*, **164**, 219 (1927).
7) E. Müller and K. Gäbler, *Z. analyt. Chem.*, **62**, 29 (1923).

TABLE I

Expt. No.	Gms. of $Pb(NO_3)_2$ in 250 ml.	Vol. of $Pb(NO_3)_2$=10 ml. $K_4Fe(CN)_6$ ml.	Weight of $K_4Fe(CN)_6$ By $Ce(SO_4)_2$ (g.) a	By Diphenylcarbazone (g.)	By Potentiometry (g.)
1	2.2775	16.20	0.0820	0.0820	0.0822
2	2.8060	48.80	0.3044	0.3042	0.3040
3	1.2335	35.5	0.0974	0.0973	0.0973
4	2.8060	24.3	0.1518	0.1516	0.1518
5	3.1416	19.6	0.1358	0.1356	0.1355
6	3.1126	18.6	0.2582	0.2586	0.2584
7	1.2335	14.8	0.04052	0.04054	0.3436
8	4.2162	36.7	0.3436	0.3438	0.3436

It is seen from a comparative study of the data that the above procedure yields accurate and reproducible results. It may also be mentioned that the limitation of using N/30 or even more dilute solutions of $K_4Fe(CN)_6$, inherent in Burstein's method[6] is not necessarily imposed on the present procedure. Since as a precipitant potassium ferrocyanide destroys immediately the pink or red color developed by Pb^{++} with diphenylcarbazone, the general difficulty of the unusual stability of the lead color met with in the case of other internal indicators[8] is not encountered in these titrations.

8) B. S. Evans, *Analyst*, **64**, 2 (1939).

Summary

A simple and direct method of estimating ferrocyanide by standard lead nitrate with diphenylcarbazone as an internal indicator has been described. The results are accurate and compared favorably with those obtained by other classical procedures.

The author wishes to express his sincere thanks to Professor S.S. Joshi for facilities and encouragement during the work and to the National Institute of Sciences of India for award of a research fellowship.

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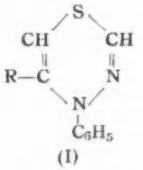
Studies on Organic Sulfur Comqounds. I. Thioformyl Phenylhydrazine

By Tadashi SATO and Masaki OHTA

(Received September 3, 1954)

Thioformylation of amine by dithioformic acid or its potassium salt was first reported by Todd.[1] He suggested that thioformamino derivatives are useful for identification of amines because of their good crystallizability and sharp melting point. He also suggested that thioacylamino derivatives could be used for the synthesis of heterocyclic compounds.

Some kinds of thioformamino- or thioformhydrazino-derivatives have been reported by one of us as intermediates for the synthesis of thiazole- or thiadiazole-derivatives.[2] Concerning our research on the synthesis of 1,3,4-thiadiazine derivatives (I) from, β-thioformyl phenylhydrazine (II), we found it necessary to investigate the properties of thioformyl phenylhydrazine.



(I)

$$C_6H_5\underset{\alpha}{N}H\underset{\beta}{N}HCHS \rightleftarrows C_6H_5NHN{=}CHSH$$

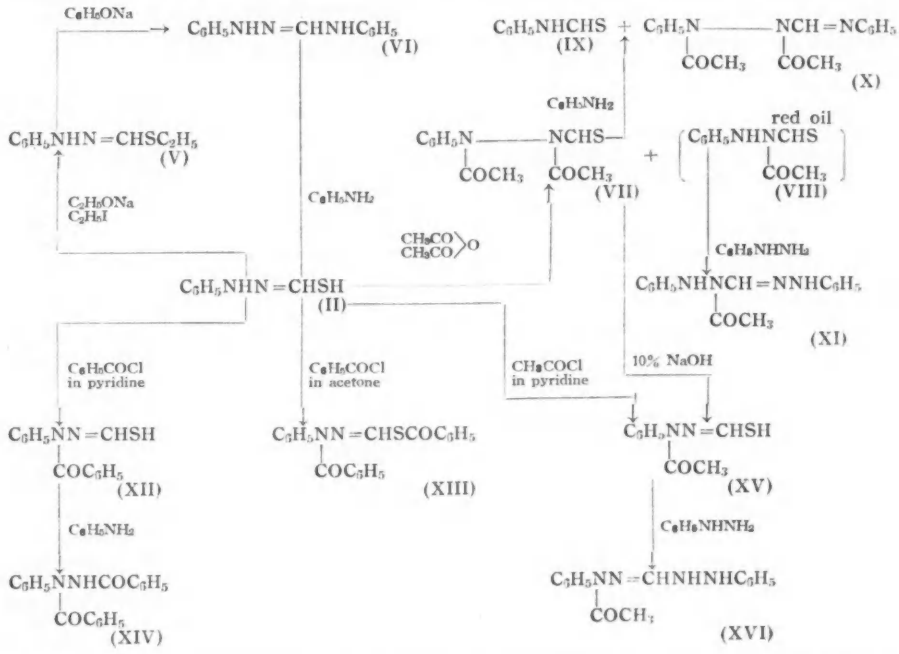
(II)

Baker et al.[3] reported the preparation of thioformyl arylhydrazine derivatives from sodium dithioformate and arylhydrazines.

1) A. R. Todd et al., *J. Chem. Soc.*, **1937**, 361.
2) M. Ohta, *J. Pharm. Soc. Japan*, **71**, 869 (1951); ibid., **73**, 701 (1953).
3) W. Baker et al., *J. Chem. Soc.*, **1950**, 3389.

They obtained (II) as an oil in a crude state and only a small portion of it became crystalline (m.p. 39-41°). They used the crude product in subsequent reactions, and concluded its structure to be (II) by analysis and several reactions. We obtained a compound (m.p. 102°) from phenylhydrazine and potassium dithioformate in a good yield. From various properties described in this report, no doubt remains that the product we obtained has a structure of (II). It is the purpose of this report to determine which hydrogen of two replaceable hydrogens of (II) is replaced, when (II) is submitted to alkylation or acylation.

When (II) was treated with sodium ethoxide and ethyl iodide, ethyl derivative (V) was obtained as an oil. (V) reacted with aniline at room temperature to afford formamidine derivative (VI) liberating ethyl mercaptan.



From this fact it is evident that the ethyl group is attached to the sulfur atom. (V) could be distilled under reduced pressure and was fiairly stable compared with the ethyl derivative of thioformyl aniline which is unstable in the presence of moisture.[4]

As for the benzoylation of (II) with one mol. of benzoyl chloride, monobenzoyl derivative (XII) was formed exclusively in pyridine solution. But when the benzoylation of (II) was carried out in acetone solution in the presence of sodium bicarbonate, the principal product was dibenzoyl derivative (XIII), and the formation of monobenzoyl derivative (XII) was small in quantity. When two mols. of benzoyl chloride were reacted with one mol. of (II) in the presence of sodium bicarbonate, dibenzoyl derivative was the sole product. (XIII) did not react with aniline even on warming, which suggests that in dibenzoyl derivative (XIII), unlike in the case of diacetyl derivative (VII), one benzoyl group must be attached to α-nitrogen atom, and the other to sulfur atom.

Monobenzoyl derivative (XII) was soluble in aqueous sodium hydroxide solution, indicating the presence of the mercapto group, so that the benzoyl group should be attached to α-nitrogen. When (XII) was heated with aniline, hydrogen sulfide was liberated and a yellow oil was obtained. From this oil some amounts of colorless crystals (m.p.177°), were obtained. It was identified as α,β-dibenzoyl phenylhydrazine (XIV) from its analytical value, melting point and mixed melting point with an authentic sample. The mechanism by which dibenzoyl phenylhydrazine is formed from monobenzoyl derivative (XII) is unknown.

The reaction of (II) with acetyl chloride

4) O. Wallach and M. Wüster, *Ber.*, **16**, 145 (1883).

gave monoacetyl derivative (XV) in pyridine solution. In the reaction of two mols. of acetyl chloride with one mole of (II) in acetone in the presence of sodium bicarbonate, the formation of diacetyl derivative had been expected on the analogy of benzoylation in the same condition. But the reaction product was a red oil and crystallization or purification were unpossible. This red oil, unlike dibenzoyl derivative (XIII), reacted with aniline to liberate hydrogen sulfide, which is supposed to be due to some by-products.

Monoacetyl derivative (XV) was also soluble in aqueous sodium hydroxide solution, so that the acetyl group should be attached to α-nitrogen and when treated with aniline at room temperature in ethanol, hydrogen sulfide was liberated but the reaction product expected could not be isolated. (XV) reacted with phenylhydrazine to give orange crystals of (XVI), melting at 188°.

When (II) was treated with acetic anhydride at room temperature, diacetyl derivative (VII) was obtained, accompanied by small quantity of red oil (VIII). (VII) was insoluble in 10% sodium hydroxide solution, but on standing, it was hydrolyzed gradually and went into solution. On acidifying with acetic acid, monoacetyl derivative (XV) was obtained. (VII) reacted with aniline liberating hydrogen sulfide and gave thioformyl aniline and (X). This fact leads us to conclude that the two acetyl groups in (VII) must be attached to α-and β-nitrogen atoms of thioformyl phenylhydrazine. The isolation of α,β-diacetyl phenylhydrazine, which should be formed in this reaction, was impossible. The red oil (VIII) obtained as by-product in acetylation of (II) with acetic anhydride, reacted with phenylhydrazine to give colorless crystals, evolving a considerable amount of hydrogen sulfide and heat. This crystal was identified as monoacetyl derivative (XI), probably an isomer of (XVI), from its analytical value. This fact shows that (VIII) must also be monoacetyl derivative and an isomer of (XV). In (XV) as well as in (XVI), it is certain that the acetyl group is attached to α-nitrogen as explained before. Consequently, in (XI) or (VIII) the acetyl group is supposed to be attached to β-nitrogen. This was also confirmed by the insolubility of (VIII) in aqueous sodium hydroxide solution.

The authors are indebted to Mr. A. Kondo for the microanalytical results reported here.

Experimental

N-Phenyl-N′-thioformylhydrazine (II). — A solution of potassium hydrosulfide was prepared by mixing a solution of potassium hydroxide (46 g. in 150 cc. of methanol) saturated with hydrogen sulfide, with a solution of 46 g. of potassium hydroxide in 150 cc. of methanol. The solution was heated to about 50° in a 3 l.-flask equipped with a long Dimroth condenser. Then 30 g. of chloroform was added and constantly shaken. An exothermic reaction occurred which led to violent boiling. After ten minutes the mixture was cooled and filtered. The filtrate was evaporated in vacuo to about 50 cc. The solution of crude potassium dithioformate thus obtained was mixed with a solution of 14 g. of phenylhydrazine in 30 cc. of methanol. The evolution of hydrogen sulfide was recognized at once. The mixture was allowed to stand overnight at room temperature, then diluted with water and acidified with acetic acid. The crystalline precipitates were collected by filtration, washed with water and dissolved in ethanol and filtered from a small amount of insoluble matter. The filtrate was diluted with water to precipitate thioformyl compounds. The crude product was purified by dissolving in dilute sodium hydroxide solution and reprecipitated by acidifying with acetic acid. Colorless leaflets resulted. m.p. 102°. Yield 17 g. (86%). Found: N, 18.21; calculated for $C_7H_8N_2S$: N, 18.41%.

N-Phenyl-N′-ethylmercaptomethylene-hydrazine (V).—To a solution of 5 g. of thioformyl phenylhydrazine in 15 cc. of ethanol were added 15 cc. of sodium ethylate solution (containing 0.8 g. of sodium) and then 5 g. of ethyl iodide at room temperature. After standing overnight at room temperature, most of the alcohol was evaporated under reduced pressure, water was added and extracted with ether. After drying over anhydrous sodium sulfate, ether was evaporated. A small portion of the residual oil was distilled under a pressure of 8 mmHg (bath temperature was 170—180°) and used for analysis. Found: C, 60.47; H, 6.36; calculated for $C_9H_{12}N_2S$: C, 60.00; H, 6.67%.

Benzoylation of (II). (*a*) *in pyridine.*—To a solution of 10 g. of thioformyl phenylhydrazine in 50 cc. of pyridine was added dropwise 9.5 g. of benzoyl chloride in a period of one hour, stirring continuously and cooling with ice-water. After standing overnight at room temperature, water was added, then the oil which soon solidified separated. Recrystallization from ethanol yielded 6 g. of light yellow crystals of N-phenyl-N-benzoyl-N′-mercaptomethylene-hydrazine (XII), melting at 140°. Found: C, 65.75; H, 4.91; N, 10.60; calculated for $C_{14}H_{12}N_2OS$: C, 65.63; H, 4.69; N, 10.93%.

(*b*) *In acetone with two mols. of benzoyl chloride.*—To a solution of 3 g. of thioformyl phenylhydrazine (1 mol.) in 30 cc. of acetone, 4 g. of sodium bicarbonate (2 mols.) were suspended, and 5.5 g. of benzoyl chloride (2 mols.) were added dropwise with constant stirring and cooling. During the addition, the product separated gradually. Stirring was continued for six hours at room temperature and the precipitates were collected by filtration, washed first with aqueous solution of sodium bicarbonate and then with water (yield, 6 g.). When recrystallized from ethanol, fine

needles of N-phenyl-N-benzoyl-N′-benzoylmercaptomethylene-hydrazine (XIII), melting at 137°, were obtained. Found: N, 7.64; calculated for $C_{21}H_{16}N_2O_2S$: N, 7.77%.

(c) *In acetone with one mole of benzoyl chloride.*—To a solution of 3 g. of thioformyl phenylhydrazine (1 mol.) in 30 cc. of acetone were added 2.5 g. of benzoyl chloride (1 mol.) in the presence of 1.7 g. of sodium bicarbonate (1 mol.) in the same manner as described above. After standing overnight the solid was collected and washed with 10% aqueous sodium hydroxide solution. The greater part of the solid was insoluble but when alkali washings were acidified with acetic acid some amounts of solid were obtained, which were identified as monobenzoyl derivative (XII) after the recrystallization from ethanol. The solid which was insoluble in alkali was dibenzoyl derivative (XIII).

Reaction of (XII) with Aniline.—To a solution of 2 g. of (XII) in 40 cc. of ethanol, 0.8 g. of aniline was added and refluxed for four hours. Addition of water to the cooled reaction mixture gave an oil, which was taken up in ether and after drying over anhydrous sodium sulfate, the ether was evaporated. From the residual oil small amounts of crystals were obtained. Recrystallization afforded colorless crystals, melting at 177°. The mixed melting point with authentic sample of N,N′-dibenzoyl phenylhydrazine (XIV) was also 177°. Found: N, 9.28, calculated for $C_{20}H_{16}N_2O_2$: N, 8.86%.

N-Phenyl-N-acetyl-N′-mercaptomethylene-hydrazine (XV).—To a solution of 5 g. of thioformyl phenylhydrazine in 30 cc. of pyridine was added dropwise 2.5 g. of acetyl chloride during a period of one hour, stirring continuously and cooling with ice-water. After standing overnight at room temperature, water was added, then the oil which soon solidified separated. Recrystallization from ethanol yielded 3 g. of light red rhombic crystals (XV), melting at 120–2° to red liquid. Found: N, 14.35; calculated for $C_9H_{10}N_2OS$: N, 14.43%.

N-Phenyl-N-acetyl-N′-phenylhydrazino-methylene-hydrazine (XVI). — To a solution of 1 g. of (XV) in 20 cc. of ethanol 0.6 g. of phenylhydrazine was added at room temperature. The reaction proceeded with liberation of hydrogen sulfide. After an hour water was added and the crystalline precipitates which separated were recrystallized from ethanol. Orange crystals of (XVI), m.p. 188° resulted. Yield, 0.5 g. Found: N, 20,56; calculated for $C_{15}H_{16}N_4O$: N, 20.90%.

N-Phenyl-N,N′-diacetyl-N′-thioformylhydrazine (VII). — Five grams of thioformyl phenylhydrazine were dissolved in 30 cc. of acetic anhydride, the temperature of the solution being kept under 30° by external cooling with water. After standing overnight at room temperature, water was added to decompose the excess of acetic anhydride. A viscous oil which soon solidified was separated. The solid was collected on the filter, and washed with ether. The crude product weighed 7 g., and melted at 103–4°. Recrystallization from ethanol yielded 6 g. of (VII) as yellow rhombic crystals melting at 107°. Found: N, 11.85; calculated for $C_{11}H_{12}N_2O_2S$: N, 11.86%.

N^{α}-Acetyl-N^{β}, $N^{\beta'}$-diphenyl-formhydrazidine (XI).—From the ether washings in the above reaction, ether was evaporated. The ethanol solution of the residual red oil was treated with phenylhydrazine at room temperature. The reaction proceeded with evolution of hydrogen sulfide and heat. After a little while water was added and the separated solid was recrystallized from dilute ethanol. Colorless needles of (XI), melting at 173° resulted. Found: C, 66.89; H, 6.09; N, 20.41; calculated for $C_{15}H_{16}N_4O$: C, 67.16; H, 5.97; N, 20.90%.

Reaction of (VII) with Aniline.—To a solution of 1 g. of (VII) in a small volume of acetone 0.4 g. of aniline was added and the mixture was kept standing at room temperature for one hour. On addition of water a colorless solid was separated. Recrystallization from dilute ethanol gave 0.3 g. of thioformyl aniline, melting at 140°, which was confirmed by its mixed melting point with authentic sample and analytical value. (Found: N, 10.02, calculated for C_7H_7NS: N, 10.21%.) Addition of water to the mother liquor of the recrystallization gave still greater amounts of solid. This was washed witn 10% sodium hydroxide solution to remove thioformyl aniline, and the residue, on recrystallization from dilute ethanol afforded colorless crystals of N,N′-diacetyl-N′-phenyl-hydrazinomethyleneaniline (X), melting at 135°. Found: N, 14.2; calculated for $C_{17}H_{17}N_3O_2$: N, 14.23%.

Hydrolysis of Diacetyl derivative (VII) into Monoacetyl derivative (XV). — One gram of diacetyl derivative (VII) was suspended in 3.5 cc. of 10% sodium hydroxide solution, and stirring was continued until dissolution was completed. Decolorizing with charcoal and acidifying with acetic acid gave an oil which soon solidified. Recrystallization from ethanol yielded colorless rhombic crystals, melting at 120–1°. Mixed melting point with monoacetyl derivative (XV) showed no depression.

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Additions and Corrections

Volume 26, 1953

T. Ishikawa: An Equation of State in Analytical Form.

Page 82. In relation (9), for "$\log_e V_c$" read "$\log V_c$".

K. Sugino and S. Aoyagi: Studies on the Mechanism of the Electrolytic Formation of Perchlorate. I.

Page 187. In col. 1, line 25–29, figures (volt) of the potential.

for "about 2.1 V" read "about 2.3 V".
for "about 2.1 V" read "about 2.3 V".
for "about 2.2 V" read "about 2.5 V".
for "about 2.4 V" read "about 2.6 V".
for "about 2.4 V" read "about 2.7 V".

In Fig. 3, in the ordinate for "Cu‡ent" read "Current". 0.25 V must be added to each figures (volt) of anodic potential in the abscissa. Erroneous figures corresponded to the values of anodic potential vs. S.C.E. Corrected figures corresponds to the values of anodic potential vs. hydrogen scale. The successive paper of this item will be published in the Journal of the Electrochemical Society.

T. Ishikawa: Application of the New Equation of State to the Joule-Thomson Effect.

Page 530. In col. 1, line 13, for "$p+a/V^{2-}$" read "$p+a/V^{2-\varepsilon}$". In col. 2, in formula (2), for "Cp" read "C_p".

Additions and Corrections

Volume 27, 1954

T. Ishikawa: An Equation of State in Analytical Form.

Page 226. In col. 1, line 16, for "For the author's curve (2-ε) the value" read "For the author's curve, the (2-ε) value".

Page 227. In Table I, for all of "H" read "γ".

S. Kawasumi: Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. V.

Page 254. In the subject for "in the Presence of Excess Am" read "in the Presence of Excess Am-". In col. 2, line 4, for "yield of Urea" read "yield of urea". In Fig. 1, for "**Symbol Starting Materil**" read "**Symbol Starting Material**".

Page 255. In col. 1, line 3, for "$Y_a+L=2Y_c$ is" read "$Y_a+L=2Y_c$, is". In Fig. 2 and Fig. 3, for "N_{urea}" read "n_{urea}".

Page 256. In Table I,

for "R.....0.925 3.380 3.827 4.390"
Y_c .....0.517 0.551 0.577 .0604"
read "R.....2.925 3.380 3.827 4.390"
"Y_c .....0.517 0.551 0.577 0.604"

and for "" read ""

Concentration. mole/l.	n'_{CO_2}	n'_{CO_2}
	n'_{NH_3}	n'_{NH_3}
	n'_{H_2O}	n'_{H_2O}
	n_{CO_2}	n_{CO_2}
	n_{NH_3}	n_{NH_3}
	n_{urea}	n_{urea}
	n_{H_2O}	n_{H_2O}
Equilibrium mole fraction	N'_{CO_2}	N'_{CO_2}
	N'_{NH_3}	N'_{NH_3}
	N'_{H_2O}	N'_{H_2O}
	N_{CO_2}	N_{CO_2}
	N_{NH_3}	N_{NH_3}
	N_{urea}	N_{urea}
	N_{H_2O}	N_{H_2O}
	$K_{N\text{-}(1)}$	$K_{N\text{-}(1)}$

Page 259. In col. 2, line 1, for "of the reaction(1)" read "of the reaction (1)" and line 23, for "X_t" read "x_t".

K. Yamamoto und M. Oku: Über die Herstellung von Styrol und Benzol aus Acetylen.

Page 385. In Fig. 1, the figure should be turned upside down.

K. Yamamoto, Y. Hirusawa und M. Yoshimura: Kupferchromit als Katalysator bei der Propargylalkoholsynthese.

Page 388. In col. 2, line 9 from the bottom, for "Ein Hälfte" read "Eine Hälfte".

K. Yamamoto und K. Sato: Über die neue synthetische Methode von Carbonsäuren durch Carbonylierung von aromatischen, halogenierten Kohlenwasserstoffen.

Page 389. In the subject for "von Carbonäsuren durch" read "von Carbonsäuren durch".

Page 390. In col. 2, line 11, for "Säuren zurück" read "Säuren zurück-". In Table, col. 2, for "Ronstoff" read "Rohstoff".

R. Okawara: Alkylalkoxypolysiloxanes. I.

Page 428. In col. 1, line 24, for "ethyldiethoxychlorosilanes" read "ethylethoxychlorosilanes". In reference (3), for "S. Numa" read "Y. Numa" and for "Svc." read "Soc.," In col. 2, line 5, for "ethylmethoxy-, and" read "ethylmethoxy- and".

A. Inoue, M. Sugiura and Y. Tsuzuki: On the Synthesis of 8-Hydroxyquinoline.

Page 430. In col. 1, line 22 from the bottom, for "metal irons," read "metal ions," and line 7 from the bottom, for "as its" read "at its".

Page 431. In col. 1, line 10 for "8-sulfoxuinoline" read "8-sulfoquinoline" and line 12 from the bottom, for "$C_9H_5NSO_3Na$" read "C_9H_5NONa". In reference (4), for "Claus, Stelzner J. prakt. Chem., [2], **53,** 390 (1896)" read "La Costc and Valeur, *Ber*, **20,** 95 (1887)".

Page 432. In col. 1, line 18, for "8-hydroxyquinolinate" read "8-hydroxyquinolinolate" and line 20, for "power on" read "powder on".

H. Tadokoro, S. Seki and I. Nitta: The Densities of Polyvinyl Alcohol Film at moist States.

Page 451. In authors' names, for "Hiroshi Tadokoro, Syuzo Seki" read "Hiroyuki Tadokoro, Syûzô Seki". In col. 1, line 14, for "there, is," read "there is,". In reference (5), for "Ann, Report Inst· Fiber" read "Ann. Report Inst. Fiber". In col. 2, line 18 from the bottom, for "fiotation medium" read "flotation medium".

Page 452. In col. 1, line 10, for "of th" read "of the". In col. 2, line 6, for "respectivery" read "respectively".

Page 453. In Fig. 5, the ordinate on the right hand side shows "$dv/d\phi$ cc./g. Å". In col. 2, line 9, for "φ" read "ϕ,", line 12, for "substance[3,4]" read "substances[3,4]", line 4 from the bottom, for "candot" read "cannot". In Table I, col. 3, for "Wathr" read "Water". In reference (14), for "S. Shuttleworth," read "R. Shuttleworth,".

Page 454. In col. 1, line 3, for "waals" read "Waals". In col. 2, line 25, for "date" read "data".

S. Yamada: Action of *p*-Toluenesulfonyl Chloride as the Cold-setting Accelerator for Thermosetting Resins.

Page 479. In col. 2, line 5, line 12 and line 1 in Fig. 1., for "resistivity" read "resistance". In Fig. 1., in the ordinate, for "($\times 1000$)" read "($\times 1000\Omega$)".

H. Tsubomura: The Nature of the Hydrogen-Bond. I. The Delocalization Energy in the Hydrogen-Bond as Calculated by the Atomic-orbital Method.

Page 446. In formula (1). In the first column; in the second formula, for "$\sqrt{2}/3x$" read "$(\sqrt{2/3})x$", in the third formula, for "$z/\sqrt{12}=y\sqrt{2}$" read "$z/\sqrt{12}+y/\sqrt{2}$", in the fourth formula, for "$-y\sqrt{2}$" read "$-y/\sqrt{2}$." In the second column, in the last formula, for "y" read "y'".

Page 446. In Col. 2, line 5 from the bottom, for "electrous" read "electrons".

Page 447. In Col. 2, line 20, for "cul-" read "cal-".

Page 449. In Col. 2, line 8, for "used" read "use", in the subtitle, for "Cahrge" read "Charge".

Page 450. In Appendix, in the middle column, line 4 from the bottom, for "(H: hs')" read "(H: hσ')".